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[Contributions from the Chemical Laboratory of Cornell University.]

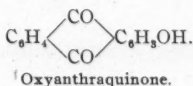
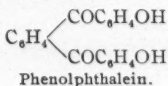
PHENOLTETRACHLORPHTHALEIN AND SOME OF ITS DERIVATIVES.¹

BY W. R. ORNDORFF AND JOHN A. BLACK.

The series of compounds formed by heating phthalic anhydride with phenols, and known as the phthaleins, were discovered by A. von Baeyer² in 1871. The reaction between phthalic anhydride and phenol he formulated as follows:



regarding phenolphthalein as analogously constituted to oxyanthraquinone:



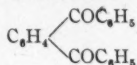
Later, in 1880,³ Baeyer and his coworkers established the constitution of phenolphthalein by showing that it could be made synthetically from diphenylphthalid, previously obtained by Friedel and Crafts by treating phthalyl chloride

¹ Read at the Baltimore meeting of the American Chemical Society.

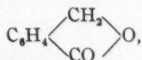
² Ber. d. chem. Ges., **4**, 659.

³ Ann. Chem. (Liebig), **202**, 36.

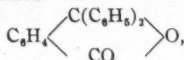
with benzene in the presence of aluminium chloride and called by them phthalophenone. Baeyer first showed that this substance did not have the structure



assigned to it by its discoverers, but that it was a diphenyl derivative of phthalid,



and had the constitution

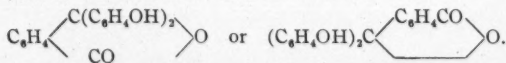


since on reduction in alkaline solution with zinc dust it gave triphenylmethanecarboxylic acid,

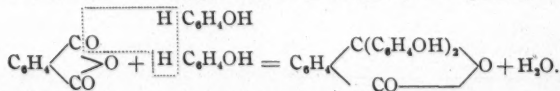


which, when heated with barium hydroxide, splits up into triphenylmethane and carbon dioxide.

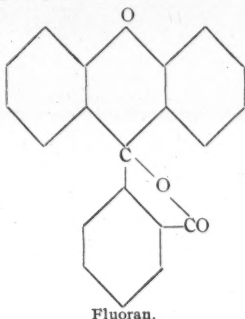
By converting this diphenylphthalid into dinitrodiphenylphthalid by the action of nitric acid, reducing to diaminodiphenylphthalid by means of tin and hydrochloric acid, and treating the diaminodiphenylphthalid in acid solution with nitrous acid he obtained a dioxydiphenylphthalid. This dioxydiphenylphthalid was found to be identical with phenolphthalein, which must therefore have the structure



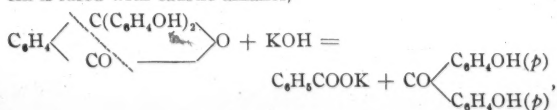
Hence, in the formation of the phthalein from phthalic anhydride it is not the anhydride oxygen which is replaced by the two phenol residues, as first supposed by Baeyer, but one of the other two oxygen atoms, as shown in the equation



As to the position of the hydroxyl groups with reference to the methane carbon atom, Baeyer considers it quite likely that they are in the para position, since phenols in which the para position is already occupied, such as *p*-chlorphenol and *p*-cresol, do not give phthaleins but derivatives of fluoran,

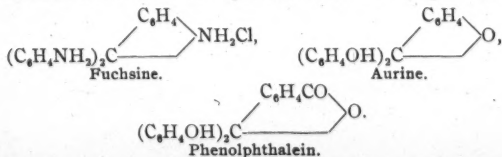


The formation of *p*-dioxxybenzophenone when phenolphthalein is fused with caustic alkalis,

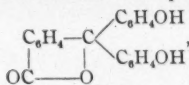


is a further proof of the para position of the hydroxyl groups in phenolphthalein.

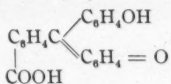
Baeyer calls attention to the very characteristic color change which takes place when phenolphthalein is dissolved in a solution of an alkali, and states that the violet color of the salts of phenolphthalein shows the close connection of these salts to fuchsine and aurine, as expressed in the following formulas:



In 1892 A. Bernthsen¹ put forward the idea that the colorless phenolphthalein has the lactone structure (I.) while the violet-red salts have the quinoid formula (II.):



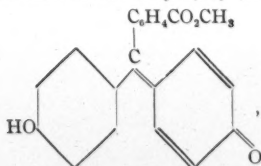
I. Phenolphthalein
(colorless).



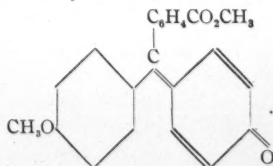
II. Phenolphthalein in its salts
(colored).

Since the publication of this paper much work has been done on the constitution of the phthaleins and their salts and it may be said that the above view is now generally accepted by chemists. The phthaleins are regarded as tautomeric substances yielding two classes of derivatives, colorless compounds having the lactoid formula (I.) and colored substances to which the quinoid structure (II.) is assigned.

Recently Green and King² have published the results of their work on the constitution of the phthalein salts, which seem to establish the above view on a firm basis. They have succeeded in preparing not only the colored, quinoid esters of phenolphthalein (I.) and of quinolphthalein, but also those of their monomethyl (II.) and dimethyl ethers:



I. Methyl ester of phenolphthalein.



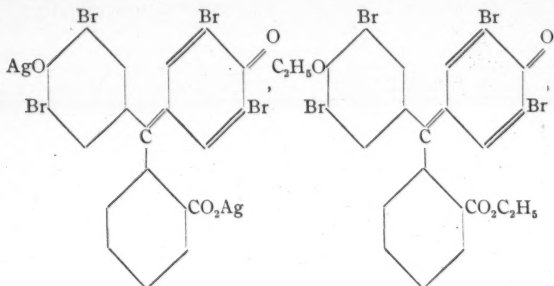
II. Methyl ester of phenolphthalein methyl ether.

These esters all possess a deep color, ranging from orange to red. They are of a high degree of instability, being saponified not only by the weakest alkalies but even by water alone. Since they were made by the ordinary method of esterification and so readily undergo saponification they must have the structure given above.

¹ Chem. Ztg., **104**, 1956.

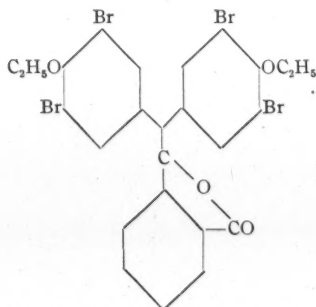
² Ber. d. chem. Ges., **39**, 2365 (1906), and J. Soc. Chem. Ind., **27**, 4 (1908).

Further proof of the quinoid structure of the salts of phenolphthalein is given by the work of R. Meyer and Marx.¹ They prepared the colored ether ester (II.) of tetrabromphenolphthalein from the blue disilver salt (I.) by treating it with ethyl iodide:



I. Disilver salt of tetrabromphenolphthalein.

II. Colored ether ester of tetrabromphenolphthalein.

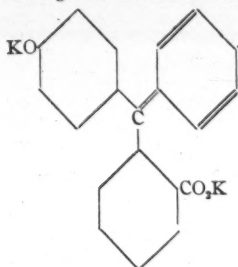


III. Colorless diethyl ether of tetrabromphenolphthalein.

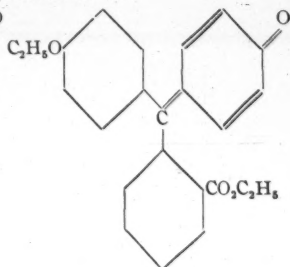
They found it impossible to obtain the colored ether ester pure, however, as it is partially converted into the colorless lactoid diethyl ether (III.) with the greatest ease on recrystallization.

¹ Ber. d. chem. Ges., 40, 1437 (1907).

tallization from various solvents. Later R. Meyer and Marx¹ prepared the red alkali salts of phenolphthalein by treating the alkali solution with an excess of the phthalein, filtering off the undissolved material, and evaporating the solution to dryness on the water bath. Analyses gave results agreeing with the formulas $C_{20}H_{12}O_4K_2$ and $C_{20}H_{12}O_4Na_2$. From the dry potassium salt (I.) they made the yellow colored quinoid ether ester (II.) by suspending it in dry benzene and heating with an excess of ethyl bromide.

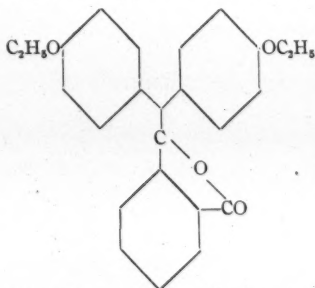


I. Red dipotassium salt of phenolphthalein.



II. Yellow diethyl ether ester of phenolphthalein.

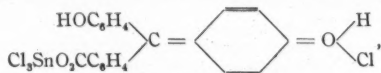
This ether ester also goes over into the colorless lactoid diethyl ether (III.) on recrystallization from solvents.



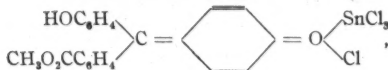
III. Colorless diethyl ether of phenolphthalein.

¹ Ber. d. chem. Ges., **40**, 3603 (1907) and **41**, 2446 (1908).

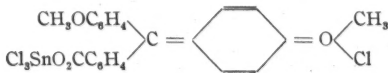
Still further confirmation of the quinoid formula for the salts of phenolphthalein is afforded by the work of K. Meyer and Hantzsch.¹ They have prepared red double salts of phenolphthalein, of the colored methyl ester, and of the colorless dimethyl ether, with aluminium chloride and with stannic chloride. They represent the structure of the compounds with stannic chloride as follows:



Red double salt with phenolphthalein.



Red double salt with the methyl ester of phenolphthalein.



Red double salt with the colorless dimethyl ether of phenolphthalein.

In 1887 Graebe,² in connection with his investigation of tetrachlorphthalic acid, made tetrachlorfluorescein and tetrachlorgallein and their acetates. He states that tetrachlorphthalic anhydride combines with phenol in exactly the same way as phthalic anhydride, but gives no details of the method for making phenoltetrachlorphthalein nor did he prepare any of its derivatives.

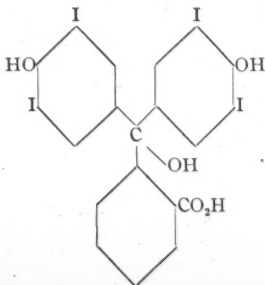
The present investigation was undertaken for the following reasons:

- (1) To ascertain the conditions under which phenoltetrachlorphthalein and its derivatives can best be made, and
- (2) To study the effect of the introduction of negative or acid groups into the molecule of phenolphthalein.

¹ Ber. d. chem. Ges., **40**, 3479 (1907).

² Ann. Chem. (Liebig), **238**, 318.

It was thought that by introducing chlorine into the phthalic acid residue in the place of the four hydrogen atoms or by making the tetrabrom or tetraiodo derivative of this phenoltetra-chlorophthalein it would be possible, owing to the acidifying influence of the halogens, to obtain a colored quinoid compound. A. Classen and W. Löb¹ have apparently made a similar compound, a hydrate of tetraiodophenolphthalein, by acidifying a strongly alkaline solution of the tetraiodophthalein, cooled to -5° , with hydrochloric acid, also cooled below 0° . The hydrate separates as a *yellowish brown* precipitate. This was filtered off, dried, dissolved in chloroform, and precipitated with ligroin. Analyses showed that it differed from the tetraiodophthalein precipitated from alkaline solution at ordinary temperatures by one molecule of water. This compound Classen and Löb designate as tetraiodophenolphthalein carbinolcarboxylic acid,



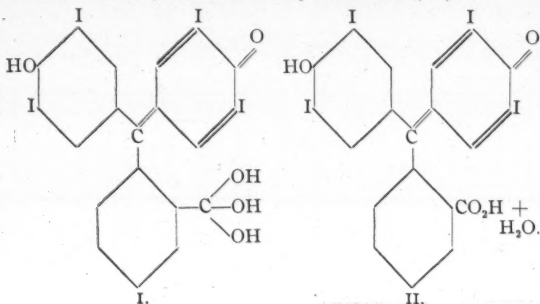
It differs from the tetraiodophthalein not only by one molecule of water, but also in that it is easily soluble in chloroform and ether. It is converted into tetraiodophenolphthalein by the loss of a molecule of water when it is heated to 100° .

As the carbinolcarboxylic acid would be a *colorless* compound according to Baeyer,² it is very probable that this hydrate is a quinoid form of the phthalein and has one of the two fol-

¹ Ber. d. chem. Ges., **28**, 1606 (1895).

² Ann. Chem. (Liebig), **354**, 152.

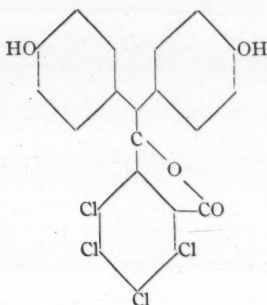
lowing structures, according as the water is regarded as water of constitution (I.) or water of crystallization (II.):



As the substance may be dissolved in chloroform and precipitated by ligroin without undergoing any change, the first formula seems the more probable one. Compounds similar to this tetraiodophenolphthalein hydrate are also known. Fluorescein hydrate, eosin hydrate, dinitrofluorescein hydrate, and tetranitrofluorescein hydrate¹ are all well-known colored compounds differing from the corresponding phthalic acids by one molecule of water, and hence they must be represented by formulas similar to the above.

It was also thought that the introduction of four atoms of chlorine into the phthalic acid residue might, in accordance with the ester rule of Victor Meyer, prevent the formation of the lactone ring, that is, the formation of an inner ester. Meyer found that substituted benzoic acids in which the substituents occupied the two ortho positions to the carboxyl group do not form esters or form them only with great difficulty by the catalytic method of esterification. Now in phenoltetrachlorophthalein both the ortho positions to the carboxyl group are occupied, and hence it ought not to form an ester very readily and might possibly not form the inner ester, *i. e.*, the lactone,

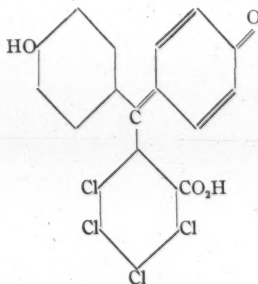
¹ As tetranitrofluorescein hydrate has a pinkish white color, according to Hewitt and Perkins (*J. Chem. Soc.*, **77**, 1330) it is probable that it is a mixture of the colored hydrate and the colorless carbinolcarboxylic acid.



Phenoltetrachlorophthalein (lactone form).

In this connection it may be mentioned that Osorowitz¹ found that tetrachlordioxyfluorescein and dichlordioxyfluorescein do not yield esters with sulphuric acid and alcohol, while dibromdioxyfluorescein does. He calls attention to the fact that in the first two compounds both ortho positions are occupied, while in the dibromdioxyfluorescein they are not; in other words, the conduct of these compounds is in accordance with the Victor Meyer rule.

It seemed likely, therefore, that phenoltetrachlorophthalein would be a colored quinoid compound,



Phenoltetrachlorophthalein (quinoid form)

¹ Ber. d. chem. Ges., **36**, 1083.

more especially since both tetrachlorfluorescein and tetrachlorgallein, which have been prepared by Graebe, are colored. It also seemed probable that phenoltetrachlorphthalein would prove to be a much stronger acid than phenolphthalein itself and that, unlike phenolphthalein, it would not be sensitive to carbonic acid. In this case it could be used as an indicator in alkalimetry and acidimetry in place of phenolphthalein and methyl orange.

EXPERIMENTAL.

Materials.—The phenol used in this investigation was Kahlbaum's pure crystallized product. This was subjected to distillation, the first fraction rejected, and only the product distilling between 180° – 181° made use of. This product, after solidifying, was perfectly white and melted sharply at 42° .

The tetrachlorphthalic anhydride was prepared from the commercial product (Kahlbaum's). It contained both the acid and the anhydride and was quite pure. It was first converted into the sodium salt, by boiling with a strong solution of sodium hydroxide, and the tetrachlorphthalic acid precipitated from the hot solution by adding an excess of hydrochloric acid. When the solution was cold, the acid was filtered off, washed with cold water, and again crystallized from hot water. This method of purification gave pure tetrachlorphthalic acid, melting at 255° – 257° (corrected), as had been previously shown by Dr. Delbridge in this laboratory by very careful analyses in connection with his work on tetrachlorphthalic acid.¹ The tetrachlorphthalic acid was then converted into the anhydride by heating it in a water oven at a temperature of about 100° for one hundred and twenty hours, previous work having shown this to be a sufficient time for its complete conversion into the anhydride. The change into the anhydride can be brought about in a shorter time at a higher temperature but with a loss of some of the anhydride, which sublimes very readily at temperatures above 100° . The zinc chloride used as a condensing agent was the C. P. article. It was freshly fused and powdered just before being used.

¹ THIS JOURNAL, 41, 393.

The sulphuric acid was also the C. P. article, 98.7 per cent, specific gravity 1.8406.

Pure fuming sulphuric acid containing 15 per cent free sulphur trioxide was also used.

Method.—The condensing agents used by Baeyer in making phenolphthalein from phenol and phthalic anhydride were fused zinc chloride, anhydrous stannic chloride, and concentrated sulphuric acid. Experiments in which all three of these substances were used separately showed that at 120° (the temperature employed by Baeyer in making phenolphthalein) only a very small yield of phenoltetrachlorophthalein was obtained. Using zinc chloride and a higher temperature the yield was not only small but the product was extremely dark in color. Stannic chloride is open to the objection that it is quite expensive, difficult to remove from the reaction products, and, as it boils at 120°, at which temperature only a small amount of tetrachlorophthalein is formed, it could not be used at a higher temperature. After many trials with concentrated sulphuric acid, specific gravity 1.8406, and with fuming sulphuric acid containing 15 per cent free sulphur trioxide, it was found that, taking into consideration the purity of the product and the yield of the phenoltetrachlorophthalein, the latter was the best condensing agent. The proportions of materials finally adopted were 100 grams of tetrachlorophthalic anhydride, 100 grams of fuming sulphuric acid containing 15 per cent of free sulphur trioxide, and 200 grams of phenol. These materials were placed in a 500 cc. round-bottomed flask, closed by a cork carrying a thermometer, and a small glass tube to act as an air condenser. The flask was then immersed in a sulphuric acid bath and heated at a temperature of 145°–150° for about 12 hours until the dark brown liquid solidified. After cooling, the flask was broken, the product separated from the broken glass, transferred to a 2-liter round-bottomed flask, and distilled with steam until the distillate ceased to give a test for phenol with bromine water. The material remaining in the flask was repeatedly boiled with water to remove any unchanged tetrachlorophthalic acid, sulphuric acid, and other soluble products. The residue was

then heated with dilute sodium hydroxide solution, which dissolved the phthalein with a red color, and the solution was separated by filtration from the tetrachlorfluoran formed as a by-product. The phenoltetrachlorphthalein was then precipitated from the filtrate with an excess of hydrochloric acid, boiled with water, filtered off on a Buchner funnel, and washed free from chlorides with hot water. This process also removed any unchanged tetrachlorphthalic anhydride which might have been present in the crude phthalein. Obtained in this way the product had a faint pink color. The average yield was 65 per cent of the calculated, that is, 65 grams of the 100 of tetrachlorphthalic anhydride used were converted into phenoltetrachlorphthalein. Tetrachlorfluoran was always formed as a by-product of the reaction, about 15 grams being obtained from 100 grams of the tetrachlorphthalic anhydride. This corresponds to a conversion of about 10 grams of the tetrachlorphthalic anhydride into tetrachlorfluoran. Of the original 100 grams of anhydride used, therefore, 65 grams were converted into phenoltetrachlorphthalein, 10 grams into tetrachlorfluoran, and 25 grams either remained uncombined or were converted into sulphonic acids of phenoltetrachlorphthalein.

Ethyl alcohol (95 per cent) and absolute methyl alcohol proved to be the best solvents for purifying the product, and repeated crystallization and boiling with bone black were necessary in order to obtain an absolutely white phenoltetrachlorphthalein. The air-dried product thus recrystallized from alcohol contains no alcohol or water of crystallization. Chlorine determinations on this product by the lime method resulted as follows:¹

	Weight of substance, gram.	Weight of silver chloride, gram.	Chlorine, per cent.
I.	0.1866	0.2364	31.32
II.	0.1876	0.2362	31.13
	Calculated for $C_{20}H_{10}Cl_4O_4$,		31.11

The substance is therefore a tetrachlor substitution product of phenolphthalein.

Properties of the Phenoltetrachlorphthalein.—The phenol-

¹ International atomic weights (1908) are used in this paper.

tetrachlorphthalein resembles phenolphthalein very closely in all its properties. It is very soluble in hot alcohol, from which it crystallizes in crystal crusts. The crystals from methyl alcohol have been examined by Professor A. C. Gill of the Mineralogical Department of Cornell University, who reports as follows:

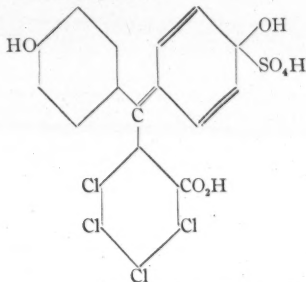
"The best crystals, obtained from solution in methyl alcohol, are nearly rectangular, colorless plates, reaching 0.5 mm. in length and about 0.2 to 0.3 mm. in breadth, with a thickness not exceeding 0.1 mm., usually about 0.05 mm. They are probably monoclinic, the large faces being the clinopinacoid, the other bounding surfaces being the base and a prism of about 54° . The angle β , as measured on the microscope stage, is approximately 93° . The extinction angle is 21° to 22° , greater optical elasticity making this angle with the vertical axis in acute β . The axial ratio $a:b = 0.51:1$. The double refraction is rather strong, giving interference colors of the higher orders in the thicker crystals.

"Since Groth found phenolphthalein to be triclinic, these crystals were carefully examined for any characteristics that might indicate that symmetry; but no divergence from parallelism in extinction could be observed when the plates were viewed through their edges, nor was any appearance of twinning detected. All evidence, therefore, is in favor of true monoclinic crystallization."

The alcoholic solution becomes milky on the addition of water and, after standing for some time, the phenoltetrachlorphthalein separates in fine needles similar to those formed when an excess of acid is added to a hot alkaline solution of the phthalein. Methyl and ethyl alcohols, acetone, ether, and glacial acetic acid dissolve the phthalein readily, while it is only slightly soluble in chloroform, benzene, and carbon bisulphide. The amorphous phthalein obtained by precipitation from a cold alkaline solution with an acid seems to be more readily soluble than the crystallized variety. In water the phenoltetrachlorphthalein is less soluble than phenolphthalein and even on boiling with water for a long time but little, if any, goes into solution. When boiled with water in soft-

glass vessels the solution takes on a faint pink color due to the solution of some of the alkali from the glass and the formation of an alkaline salt.

In concentrated sulphuric acid the phthalein dissolves readily in the cold with a reddish yellow color, probably owing to the formation of a sulphate,



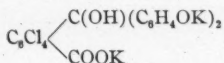
and it is precipitated unchanged from this solution by water. When the substance is heated with concentrated sulphuric acid to 120° or allowed to stand with it for 12 hours, it dissolves with the same reddish yellow color but is no longer precipitated by water, probably owing to the formation of a sulphonic acid, as this aqueous solution gives the same color changes with alkalis as the phthalein itself.

Phenoltetrachlorphthalein does not melt even when heated to 300°.

Salts of Phenoltetrachlorphthalein.—Phenoltetrachlorphthalein, like phenolphthalein, is a very weak acid and does not give well characterized salts. In the caustic alkalis or in the alkaline carbonates it dissolves very readily, forming colored solutions of the alkaline salts. In concentrated solutions the color is red, in thin layers purple, while in dilute solutions it is violet-red. In very dilute alkaline solutions the color has a bluish tint which distinguishes it from phenolphthalein.

The addition of a large excess of the caustic alkalis to the dilute alkaline solution of the phthalein decolorizes it on

standing, probably owing to the formation of the tripotassium or sodium salt of the carbinolcarboxylic acid,



The addition of acids to the violet-red alkaline solution decolorizes it at once and precipitates the phthalein, as it is practically insoluble in water. The phenoltetrachlorphthalein may therefore be used as an indicator in acidimetry and alkalimetry in the same way as phenolphthalein. Indeed we have found that for titrating organic acids it is better than phenolphthalein as the end point is sharper, and although it is sensitive to carbon dioxide, it is not so much so as phenolphthalein. It cannot be used as an indicator for titrating alkaline carbonates or alkalis in the presence of alkaline carbonates except by boiling off the carbon dioxide. An alkaline solution is not decolorized so readily by alcohol as a corresponding solution of phenolphthalein, as the following experiment made for us by Dr. T. G. Delbridge shows:

A. *Phenolphthalein* (mol. wt. 318).—Dissolved 0.0032 gram in 10 cc. of alcohol, diluted to 100 cc. with distilled water, and added 2.5 cc. of N/100 sodium hydroxide solution.

Color, light red, decidedly lighter than B.

Added alcohol until the solution was completely decolorized. Required 10 cc. of alcohol.

2 cc. of N/100 sodium hydroxide solution were then added to the colorless solution.

Color, light red.

B. *Phenoltetrachlorphthalein* (mol. wt. 456).—Dissolved 0.0046 gram in 10 cc. of alcohol, diluted to 100 cc. with distilled water, and added 2.5 cc. of N/100 sodium hydroxide solution.

Color, deep red, decidedly deeper than A.

Added alcohol until the solution was completely decolorized. Required 30 cc. of alcohol.

2 cc. of N/100 sodium hydroxide solution were then added to the colorless solution.

Color, reddish purple.

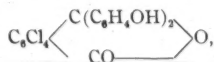
The alcohol used was 94 per cent by volume and was distilled from sodium hydroxide previous to being used to remove acids. The distilled water was boiled to remove carbon dioxide. Phenoltetrachlorphthalein is therefore preferable to phenolphthalein as an indicator for titrating alcoholic solutions. No salt is precipitated from an alkaline solution by alcohol nor was it possible to precipitate a sodium salt by treating a solution of sodium ethylate in alcohol with an excess of the phthalein dissolved in alcohol. Ammonia dissolves the phthalein with the same color as the caustic alkalies. On boiling this solution the ammonia is driven off and the color gradually becomes fainter and finally disappears, the phthalein being reprecipitated. The free phthalein does not form an ammonium salt when placed in a desiccator over a concentrated solution of ammonia, nor when treated with dry ammonia gas. Calcium hydroxide and barium hydroxide solutions also dissolve the phthalein with a red color.

The disodium salt was made by dissolving 4.56 grams of the phthalein in alcohol, adding a solution of exactly 0.46 gram of sodium in alcohol, and evaporating to dryness on the water bath. The red disodium salt thus obtained dissolves in water or alcohol with a red color. In dilute aqueous solution it undergoes hydrolysis to a considerable extent, especially when the solution is boiled, as is shown by the precipitation of phenoltetrachlorphthalein and the fact that the solution loses almost all its color.

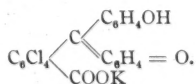
An attempt was made to prepare double salts of the tetrachlorphthalein with stannic and aluminium chlorides according to the method of K. Meyer and Hantzsch. It was dissolved in nitrobenzene and treated with the calculated quantity of aluminium chloride or anhydrous stannic chloride, also dissolved in nitrobenzene. When this mixture was poured into carbon disulphide, nothing but unchanged phenoltetrachlorphthalein was precipitated. Unlike phenolphthalein, therefore, the phenoltetrachlorphthalein does not form double salts with either stannic or aluminium chlorides. It also does not combine with hydrochloric acid gas to form a hydrochloride.

Attempts to make a monomethyl ester or a monomethyl

ester hydrochloride according to the method of Green and King, by dissolving the phthalein in absolute methyl alcohol saturated with zinc chloride or containing 100 per cent sulphuric acid and passing in dry hydrochloric acid gas, were unsuccessful. Neither the methyl ester nor the hydrochloride of the ester could be isolated, although, judging from the deep red color of the solution, they may have been formed. This is in conformity with the ester rule of Victor Meyer. The converse of the Meyer rule, that esters of diortho substituted acids are not saponified at all or only with great difficulty, does not seem to hold here. Phenoltetrachlorphthalein must have the structure of a lactone, since it is a colorless compound and gives a colorless diacetate and a colorless dimethyl ether. That is, it is an *inner ester*, as shown in the formula



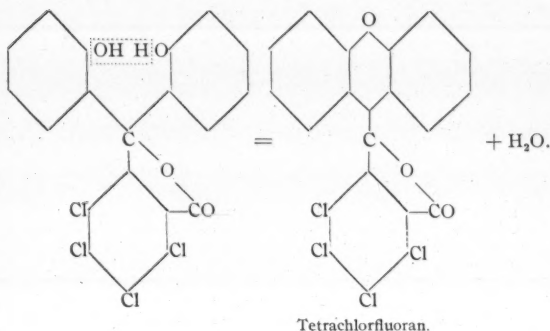
and yet the slightest trace of even the weakest base is sufficient to break up this lactone ring (saponify the inner ester), and give a salt of the phthalein



Phenoltetrachlorphthalein, like phenolphthalein, acts as a mild purgative. The physiological action is being investigated by Professor J. J. Abel, of the Johns Hopkins University.¹

Tetrachlorfluoran.—This substance is analogous in every respect to fluoran and is formed in a similar manner as a by-product in the preparation of phenoltetrachlorphthalein. As in the case of the formation of fluoran the phthalic acid residue here enters the two phenol molecules in the ortho positions to the hydroxyl groups and at the same time the two phenol hydroxyl groups lose a molecule of water:

¹ J. Pharmacology and Exp. Therapeutics, Vol. 1, No. 2.



The average yield of the tetrachlorfluoran was 15 grams from the 100 grams of tetrachlorphthalic anhydride used.

The crude product, separated from the phenoltetrachlorphthalein, was boiled with dilute sodium hydroxide solution, filtered, washed thoroughly with hot water till the wash water ran through colorless, and again boiled with dilute sodium hydroxide solution. This process was repeated as long as the material imparted any color to the alkaline solution, *i. e.*, as long as it contained any phenoltetrachlorphthalein. It was then filtered off, washed, dried, and crystallized from benzene, bone black being used to decolorize the benzene solution. After filtering off the bone black and evaporating some of the benzene, colorless crystals of the tetrachlorfluoran separated. These were filtered off, washed with benzene, dried in the air, and analyzed, a modification of the lime method which had been found to be of great value in the investigation of tetrachlorgallein being used. This modification consists in heating the substance with lime in the usual way, dissolving the mass in dilute nitric acid in an Erlenmeyer flask, adding a measured excess of standard silver nitrate solution, closing the flask with a rubber stopper, and shaking the contents vigorously for a few minutes. The silver chloride, mixed with the carbonaceous material and insoluble

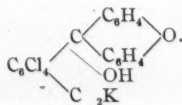
matter from the lime, is then filtered off and thoroughly washed, and the excess of silver nitrate in the filtrate determined with a standard solution of ammonium sulphocyanate, ammonium ferric sulphate being used as an indicator. The standard silver nitrate solution used was exactly tenth-normal, that is, 1 cc. was equivalent to 0.003545 gram of chlorine. This method of determining chlorine is very accurate and rapid and was used in most of the analyses. The results of the analyses of tetrachlorfluoran were as follows:

	Weight of substance, gram.	N/10 silver nitrate, cc.	Chlorine, per cent.
I.	0.1812	16.53	32.34
II.	0.1926	17.58	32.36
	Calculated for $C_{20}H_8Cl_4O_3$,		32.38

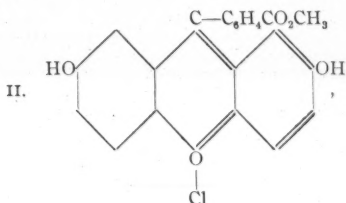
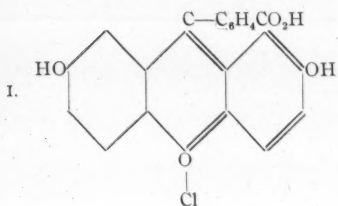
Tetrachlorfluoran is soluble in alcohol, benzene, and glacial acetic acid from which solutions it may be obtained in crystals. The crystals from benzene were examined by Professor Gill, who reports as follows:

"The stout, colorless, prismatic crystals are probably triclinic. They are optically biaxial, with *very* strong double refraction and an extinction angle which reaches about 35° as a maximum."

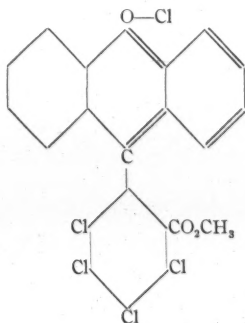
Tetrachlorfluoran is not acted upon by aqueous solutions of the caustic alkalis even on boiling. It dissolves in a concentrated solution of alcoholic caustic potash, probably forming a salt of the carbinolcarboxylic acid,



We attempted to prepare an ester or an ester hydrochloride of this carbinolcarboxylic acid by the method of Green and King. These authors prepared the hydrochloride (I.) and red methyl ester hydrochloride (II.) of quinolphthalein, to which they assign the formulas



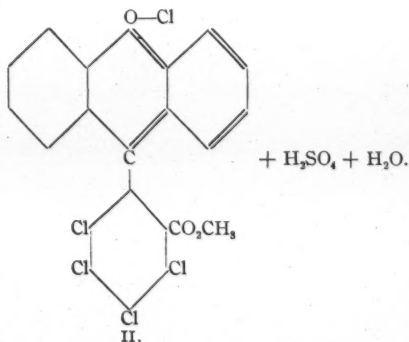
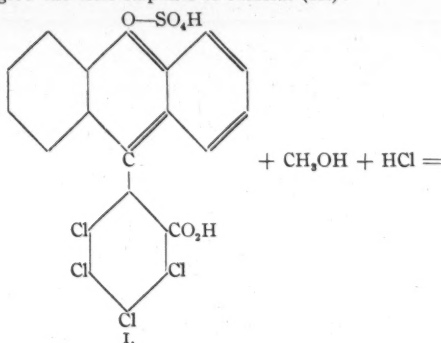
representing them as having the orthoquinoid structure and as oxonium salts. It seemed possible, if the above formulas are correct, that we might obtain a methyl ester hydrochloride of tetrachlorfluoran having the structure



Five grams of the tetrachlorfluoran were dissolved in absolute methyl alcohol, a saturated methyl alcoholic solution

of zinc chloride was added, and dry hydrochloric acid gas then passed into the boiling alcoholic solution for four hours. No change in color took place. The alcohol was then evaporated and the residue treated with water. Unchanged tetrachlorfluoran was recovered. No reaction had taken place.

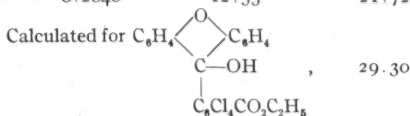
In another attempt the tetrachlorfluoran was dissolved in concentrated sulphuric acid, the solution diluted with absolute methyl alcohol, and dry hydrochloric acid gas passed into the boiling mixture for four hours. It was thought that the oxonium sulphate (I.) would be formed first and that this would give the ester sulphate or chloride (II.):



On distilling off the alcohol and treating with water only tetrachlorfluoran was obtained. An attempt to make the ethyl ester by treating a solution of the fluoran in alcoholic caustic potash with ethyl iodide also failed to give the product sought for. Five grams of the tetrachlorfluoran were dissolved in absolute alcohol and treated with one gram of caustic potash dissolved in absolute alcohol. An excess of ethyl iodide was then added and the mixture boiled for eight hours on a water bath in a flask connected with a reflux condenser. The alcohol was then evaporated off on the water bath and the residue treated with water to remove potassium iodide. The residue was crystallized several times from alcohol.

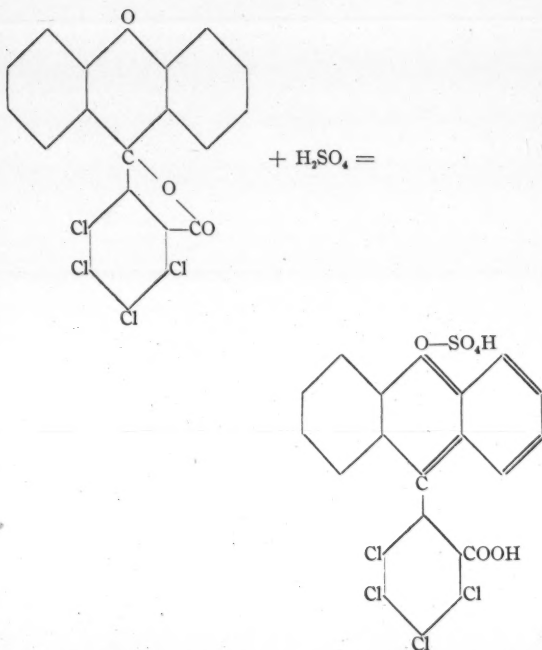
Analyses gave the following results:

	Weight of substance, gram.	N/10 silver nitrate, cc.	Chlorine, per cent.
I.	0.2562	15.70	21.72
II.	0.2048	12.55	21.72



Chlorine has been removed and the product is not a derivative of tetrachlorfluoran. It dissolves in concentrated sulphuric acid with a yellow color but shows no fluorescence. Water reprecipitates the product unchanged.

Tetrachlorfluoran dissolves in concentrated sulphuric acid and in fuming nitric acid with a marked greenish yellow fluorescence and is precipitated unchanged from these solutions by water. It is possible that the color of these solutions is due to the formation of orthoquinoid oxonium nitrate or sulphate, having a structure analogous to Green and King's quinalphthalein hydrochloride:



Attempts to prepare a colored hydrochloride of tetrachlorfluoran were unsuccessful. The fluoran does not melt even when heated to 300° .

Phenoltetrachlorophthalein Diacetate.—Ten grams of pure phenoltetrachlorophthalein, ten grams of freshly fused sodium acetate, and fifty grams of Kahlbaum's pure acetic anhydride, were heated to boiling for one hour on a sand bath in a round-bottomed flask connected with a reflux condenser, the flask being shaken constantly to prevent charring of the materials. The warm liquid was then poured into one and a half liters

of water containing ice. The diacetate separated as an oil. After solidification the diacetate was filtered off on a Buchner funnel with the aid of suction and washed free from acetic acid and sodium acetate. The conversion of the phthalein into the diacetate was practically quantitative, a yield of 97 per cent of the calculated being obtained. The diacetate was recrystallized from benzene and obtained in a pure condition. Well-formed colorless crystals of the pure product were obtained by recrystallizing from absolute alcohol. These were examined by Professor Gill who reports as follows:

"The crystals are monoclinic, elongated in the direction of the ortho-axis, with an angle β of about 84° . Very variable measurements of the two end faces gave about 52° as their probable angle with the faces in the long zone. The double refraction is extremely high, and the extinction is parallel."

The air-dried product gave the following results on analysis:

	Weight of substance, gram.	Weight of silver chloride, gram.	Chlorine, per cent.
I.	0.1951	0.2070	26.23
II.	0.2027	0.2158	26.32
	Calculated for $C_{20}H_8Cl_4O_4(C_2H_5O)_2$,		26.27

The number of acetyl groups was then determined by a modification of the Wenzel method.¹ The diacetate was heated with 10 cc. of sulphuric acid (3:1), first on the water bath and then to boiling. After the addition of 25 cc. of the phosphate mixture the solution was distilled in steam, a Vigreux tube being used to prevent any mineral acid from being carried over mechanically. The 500 cc. of the distillate were titrated with tenth-normal potassium hydroxide solution, phenolphthalein being used as the indicator. This solution, acidified with hydrochloric acid, was then titrated with tenth-normal iodine solution to determine the sulphur dioxide present. This volume of the iodine solution was subtracted from that of the alkali, thus giving the corrected amount of the potassium hydroxide solution required to neutralize the acetic acid.

The analysis was made by Mr. H. W. Gillett.

¹ Monatsh. Chem., 18, 659.

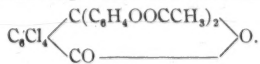
Weight of substance, gram.	N/10 iodine solution cc.	N/10 KOH solution (corrected), cc.	C ₂ H ₅ O, per cent.
0.296	0.10	10.9	15.84
	Calculated for C ₂₀ H ₈ Cl ₄ O ₄ (C ₂ H ₅ O) ₂ ,		15.94

Hence the product contains two acetyl groups.

The diacetate of phenoltetrachlorphthalein resembles the diacetate of phenolphthalein very closely in its properties. It is soluble in benzene, alcohol, and glacial acetic acid. It is saponified very slowly by cold aqueous alkalis or dilute sulphuric acid. Heating accelerates the saponification. Alcoholic solutions of the caustic alkalis saponify it readily, especially on heating, and the free tetrachlorphthalein may be obtained perfectly pure by neutralizing the solution with dilute acids and distilling off some of the alcohol. It is saponified at once by concentrated sulphuric acid.

The pure diacetate melted at 205°–206°.

As it is a colorless compound, it must have the structure



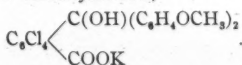
The Ethers of Phenoltetrachlorphthalein.

The Dimethyl Ether of Phenoltetrachlorphthalein.—Pure phenoltetrachlorphthalein (9.1 grams) was dissolved in pure absolute methyl alcohol and treated with about 1 gram of sodium dissolved in absolute methyl alcohol. An excess of methyl iodide was then added and the mixture was heated for one hundred and twenty hours in a round-bottomed flask connected with an upright condenser. A solution of 1 gram of sodium in methyl alcohol and methyl iodide was added from time to time as the red color of the solution disappeared. This excess of sodium methylate was added for the purpose of saponifying the colored ether ester and converting it into the sodium salt of the mono-methyl ether, which was then transformed by the methyl iodide into the colorless dimethyl ether. When the addition of the sodium methylate no longer gave any color or only a faint pink color, the methyl alcohol and excess of methyl iodide were distilled off on the water bath and the residue remaining

in the flask was treated with water to remove the sodium iodide. The insoluble product was filtered off, washed with water, and dried. It contained the colorless dimethyl ether, a small quantity of the colored dimethyl ether ester, and some monomethyl ether. It was therefore boiled repeatedly with dilute sodium hydroxide solution for the purpose of removing any ether ester (by saponification), and monomethyl ether, together with any unchanged tetrachlorphthalein which might have been present. The residue was then filtered off, washed thoroughly with water, dried, and recrystallized twice from ethyl alcohol to obtain a perfectly pure, colorless product. Some of these crystals from alcohol were examined by Professor Gill who reports as follows:

"The crystals of the dimethyl ether of phenoltetrachlorphthalein are doubtless triclinic, usually in the shape of flattened needles or prisms. Optically they show an extinction angle of 0° to 6° with the long diameter, with the greater optical elasticity in this direction. The crystals are biaxial with a double refraction of 0.035 or more. On some crystals the two end faces were seen to make angles of 56° and 46° , respectively, with the direction of elongation."

The dimethyl ether is insoluble in aqueous solutions of the alkalis, but dissolves in a concentrated solution of alcoholic caustic potash without color, probably forming the potassium salt of the carbinol carboxylic acid,



In concentrated sulphuric acid the dimethyl ether dissolves with a fine red color, purple in thin layers, and it is precipitated unchanged by water. The phenoltetrachlorphthalein gives a similar color but not so intense. The color is probably due to the formation of sulphates.

Analyses of the air-dried product gave the following results:

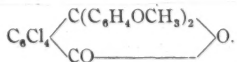
	Weight of substance, gram.	N/10 silver nitrate, cc.	Chlorine, per cent.
I.	0.1580	13.05	29.28
II.	0.1622	13.38	29.24
	Calculated for $\text{C}_{20}\text{H}_8\text{Cl}_4\text{O}_4(\text{CH}_3)_2$,		29.31

A determination of the number of methoxy-groups in this compound was made by Mr. H. W. Gillett by Decker's modification of Zeisel's method, the volumetric¹ being substituted for the usual gravimetric method. The following result was obtained:

Weight of substance, gram.	N/10 silver nitrate, cc.	CH ₃ O, per cent.
0.2268	9.5	12.99
Calculated for C ₂₀ H ₈ Cl ₄ O ₄ (CH ₃) ₂ ,		12.82

Acetic anhydride was used with the hydriodic acid, as recommended by Herzig.²

The substance is therefore the dimethyl ether of phenol-tetrachlorophthalein. The melting point of the pure product was found to be 152°-153°. As it is a colorless compound and is not saponified by alcoholic caustic potash it must be represented by the formula



The Diethyl Ether of Phenoltetrachlorophthalein.—Attempts were made to prepare this ether by the method used in making the colorless dimethyl ether. After repeatedly extracting the product with sodium hydroxide solution it was washed with water, dried, and recrystallized a number of times from 75 per cent alcohol. The crystals were colorless and melted at 145°.

Analyses of the air-dried product gave the following results:

	Weight of substance, gram.	N/10 silver nitrate, cc.	Chlorine, per cent.
I.	0.1618	6.80	14.90
II.	0.1690	7.10	14.89
Calculated for C ₂₀ H ₈ Cl ₄ O ₄ (C ₂ H ₅) ₂ ,			27.70

From the above results it is clear that chlorine has been removed and that the product is not a derivative of phenol-tetrachlorophthalein. It was therefore not investigated further.

¹ Montash. Chem., 19, 116 (1898).

² *Ibid.*, 9, 544.

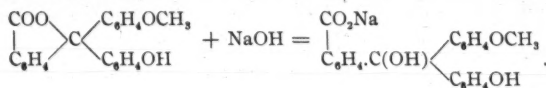
The case with which chlorine is removed from the phenol-tetrachlorphthalein is rather unexpected and surprising, especially since we had no difficulty in obtaining the colorless diethyl ether of tetrabromphenoltetrachlorphthalein by the same method.

The Monomethyl Ether of Phenoltetrachlorphthalein.—Phenoltetrachlorphthalein (9.1 grams) dissolved in absolute methyl alcohol was treated with 0.92 gram of sodium in absolute methyl alcohol and heated for three hours with an excess of methyl iodide in a round-bottomed flask connected with an upright condenser. The alcohol and excess of methyl iodide were then distilled off on the water bath, the residue extracted, first with water and then repeatedly with sodium hydroxide solution. The monomethyl ether, together with any unchanged phenoltetrachlorphthalein which was present, were then precipitated from the alkaline filtrate with hydrochloric acid. More of the monomethyl ether was obtained by saponifying a mixture of the colored ether ester and the colorless dimethyl ether with caustic potash in methyl alcohol, evaporating to dryness on the water bath, and boiling the residue with water. The potassium salt of the monomethyl ether went into solution while the colorless dimethyl ether remained undissolved. After filtering the alkaline solution the monomethyl ether was precipitated with hydrochloric acid, washed, and dried. To remove any phenoltetrachlorphthalein the product was treated several times with cold chloroform in which the tetrachlorphthalein is not very soluble. After filtering, the chloroform solution was evaporated to dryness on the water bath and the residue was crystallized from dilute acetone. Colorless crystals were obtained which, after drying in the air, gave the following results on analysis:

	Weight of substance, gram.	N/10 silver nitrate, cc.	Chlorine, per cent.
I.	0.2257	19.25	30.24
II.	0.1777	15.18	30.28
	Calculated for $C_{20}H_{10}Cl_4O_4CH_3$,		30.18

The monomethyl ether is extremely soluble in benzene and chloroform, which distinguishes it from the phthalein

itself. It is also easily soluble in acetone, methyl and ethyl alcohols, and in acetic acid. It dissolves in alkalis with a red color somewhat different from that of the alkaline solution of phenolphthalein. The lactone monomethyl ether of phenolphthalein, prepared by Meyer and Spengler,¹ also dissolves in alkalis, according to these authors, with a red color of less intensity than that produced by phenolphthalein itself. According to Green and King² this color is due to the presence of a small quantity of phenolphthalein in the monomethyl ether, since they found that the more completely they purified their monomethyl ether, the weaker was the color produced when it was dissolved in alkalis. They are of the opinion that the ether is directly converted by alkalis into the colorless carbinol salt:



Further work will be necessary to determine whether this view is correct.

Nietzki and Burckhardt³ found that the colorless monomethyl ether of tetrabromophenolphthalein also dissolves in dilute caustic alkalis without color.

In concentrated sulphuric acid the monomethyl ether of phenoltetrachlorophthalein dissolves with the same reddish yellow color as the phthalein itself and it is reprecipitated unchanged on the addition of water. It does not melt even when heated to 300°.

When boiled with acetic anhydride and sodium acetate it yields a colorless crystalline acetate. Professor Gill reports as follows in regard to the crystal from of the ether:

"The substance crystallizes from dilute acetone in colorless grains or scales with oblique extinction and medium high double refraction. The optical figure might be the obtuse bisectrix of a biaxial crystal or possibly normal to the axis of

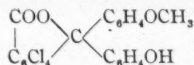
¹ Ber. d. chem. Ges., **38**, 1318 (1905).

² J. Soc. Chem. Ind., **27**, 6 (1908).

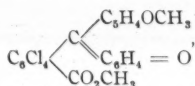
³ Ber. d. chem. Ges., **30**, 178 (1897).

a uniaxial crystal. The system is probably monoclinic or triclinic."

As it is colorless, is not saponified by alcoholic caustic potash, and yields a colorless acetate, it must have the structure



Many attempts were made to prepare the colored dimethyl ether ester,



but it was found practically impossible to obtain it free from the colorless dimethyl ether. It is formed together with the monomethyl and dimethyl ethers, has a marked yellow color, is much more soluble in alcohol and benzene than the colorless dimethyl ether, and separates from these solvents in oily drops. It is saponified by heating with an alcoholic solution of caustic potash, yielding the potassium salt of the monomethyl ether.

Tetrabromphenoltetrachlorphthalein.—This substance was made according to the directions given by Baeyer for making tetrabromphenolphthalein. Ten grams of the phenoltetrachlorphthalein were placed in a round-bottomed flask connected with an upright condenser and dissolved in 125 cc. of boiling alcohol. Thirteen and six-tenths grams of bromine dissolved in the same amount of glacial acetic acid were then slowly added through the inner tube of the condenser to the boiling solution of the phthalein. The solution was then boiled for fifteen minutes to complete the reaction, the alcohol distilled off on the water bath, and the residue treated with water. The product was then filtered off on a Buchner funnel by the aid of suction and washed free from acid. The yield of the tetrabrom product was practically quantitative. Even after repeated crystallizations from alcohol the substance did not give satisfactory results on analysis. It was therefore converted into the diacetate by the method given under

phenoltetrachlorophthalein diacetate, and this was recrystallized from benzene. Analyses of this product having shown that it was pure, it was reconverted into the tetrabromphenoltetrachlorophthalein by saponifying it in the cold with an alcoholic solution of caustic potash. When the saponification was complete the alkali was neutralized with hydrochloric acid, the alcohol distilled off, water added, and the product filtered off, washed with water, dried, and recrystallized from alcohol. The chlorine and bromine were determined in the air-dried material by the indirect method with lime with the following precautions: it was found that during the heating with lime either calcium chlorate or bromate was always formed, owing to the oxidizing action of the bromine. As silver bromate and chlorate are soluble the results for chlorine and bromine always come low. To overcome this difficulty one or two grams of sodium sulphite were dissolved in the water before the lime and nitric acid were added. On the addition of the nitric acid sulphur dioxide was set free and reduced any chlorate or bromate present to the chloride or bromide. This solution in dilute nitric acid was then filtered from carbonaceous and insoluble material from the lime, and the residue washed thoroughly with water. The chlorine and bromine in the filtrate were then precipitated with a measured excess of tenth-normal solution of silver nitrate as silver chloride and bromide. The precipitate was filtered off on a Gooch crucible, washed thoroughly, dried, and weighed. The excess of silver nitrate was then determined in the filtrate in the usual manner by titration with a standard solution of ammonium sulphocyanate, ammonium ferric sulphate being used as an indicator. Knowing the weight of the substance taken (A), the weight of the silver chloride and bromide (B), and the amount of the silver nitrate solution required to exactly precipitate the chlorine and bromine (C), the percentage of chlorine and bromine may be calculated by means of the following equations:

$$\text{Percentage of chlorine} = \frac{C - 53.224 B}{0.66822 A},$$

$$\text{Percentage of bromine} = \frac{69.745 B - C}{0.38821 A}.$$

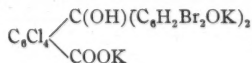
Analyses of the air-dried tetrabromphenoltetrachlorphthalein gave the following results:

	A. weight of substance, gram.	B. weight of silver halides, gram.	C. N/10 AgNO ₃ , cc.	Chlorine, per cent.	Bromine, per cent.
I.	0.1900	0.3254	19.67	18.51	41.01
II.	0.2860	0.4898	29.60	18.47	41.09
	Calculated for C ₂₀ H ₆ Cl ₄ Br ₄ O ₄			18.38	41.44

It is interesting to note that nearly 60 per cent of this compound consists of chlorine and bromine and yet the substance has the properties of phenolphthalein. It does not melt even when heated to 300°. It is soluble in alcohol and benzene and crystallizes from hot benzene in colorless crystals. These were examined by Professor Gill, who reports as follows:

"The slightly brownish crystals occur in rather thick elongated plates, triclinic in form. They show an optical axis nearly normal to the large face. Dispersion is so strong that monochromatic light would be necessary to determine the extinction angle. Double refraction is strong, optical angle large, and optical character negative."

Tetrabromphenoltetrachlorphthalein is a stronger acid than phenoltetrachlorphthalein or phenolphthalein, but like both of these substances it is sensitive to carbonic acid and hence cannot be used as an indicator in place of methyl orange in titrating carbonates. It is recommended by E. Rupp and K. Seegers¹ for titrating strongly colored solutions of the quinine bases. It dissolves in solutions of sodium, potassium, ammonium, calcium, and barium hydroxides and in the alkaline carbonates with a blue color. The addition of large amounts of the alkalis to solutions in caustic soda or potash decolorizes the solution immediately, probably owing to the formation of the trisodium or tripotassium salt of the carbinol-carboxylic acid,



An aqueous solution of the disodium salt, when treated with a solution of copper sulphate, gives a deep blue precipitate of

¹ Apoth. Ztg., 22, 748 (1907).

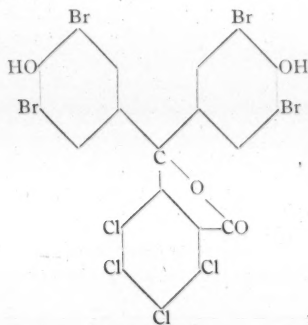
the copper salt of the phthalein. Lead acetate and silver nitrate solutions likewise give amorphous precipitates of the lead and silver salts, the lead salt having a lighter blue color than the silver salt. In cold concentrated sulphuric acid the phthalein is difficultly soluble with a yellowish red color. The addition of water discharges this color and precipitates the phthalein in an amorphous condition.

It does not form double salts with either aluminium chloride or stannic chloride.

An unsuccessful attempt was made to obtain a colored quinoid compound with the tetrabromphenoltetrachlorphthalein similar to the one from the tetraiodophenolphthalein described by Classen and Löb. Two grams of the tetrabromphenoltetrachlorphthalein were dissolved in a strong solution of sodium hydroxide and the solution cooled to 3° . On neutralizing carefully with hydrochloric acid, keeping the temperature at 3° , a colorless precipitate consisting of the tetrabromphenoltetrachlorphthalein was obtained. A colored hydrate is not formed under these conditions.

Tetrabromphenoltetrachlorphthalein does not form a methyl ester by the hydrochloric or sulphuric acid catalytic method. This is in accord with the Victor Meyer rule.

Assuming that in this compound the bromine atoms take the same positions as in the tetrabromphenolphthalein it must have the structure



since it is a colorless compound and yields a colorless diacetate and a colorless dimethyl ether.

Tetrabromphenoltetrachlorphthalein Diacetate.—The same method and same proportions of materials were used in the preparation of this substance as in the case of the diacetate of the phenoltetrachlorphthalein. The yield was practically quantitative. The crude product was recrystallized from benzene and obtained in a pure condition. Crystals were also obtained from absolute alcohol.

The following are the results of the analyses of the air-dried product by the indirect method with lime:

	A, weight of substance, gram.	B, weight of silver halides, gram.	C, N/10 AgNO ₃ , cc.	Chlorine, per cent.	Bromine, per cent.
I.	0.1612	0.2461	14.84	16.17	37.14
II.	0.1880	0.2897	17.48	16.40	37.34
	Calculated for C ₂₀ H ₄ Cl ₄ Br ₄ O ₄ (C ₂ H ₃ O) ₂ .			16.57	37.37

A determination of the number of acetyl groups present was also made by a modification of the Wenzel method.¹ The apparatus and chemicals were first tested with acetanilide with the following result:

Weight of substance, gram.	N/10 sodium hydroxide, cc.	Acetyl, per cent.
0.4160	30.46	31.49
	Calculated for C ₆ H ₅ NHCOCH ₃ .	
		31.84

With the diacetate the following result was obtained:

0.3880	9.45	10.47
	Calculated for C ₂₀ H ₄ Cl ₄ Br ₄ O ₄ (C ₂ H ₃ O) ₂ .	
		10.05

Hence the substance must be a diacetate. Professor Gill has kindly furnished the following description of the crystals:

"The crystals are probably monoclinic, flattened parallel to the plane of symmetry. β = about 88°. The double refraction is positive and very high. The obtuse bisectrix is normal to the surface of the flat plates. Dispersion is so strong as to interfere with accurate determinations of the extinction angle, which is about 20° for average wave length of light."

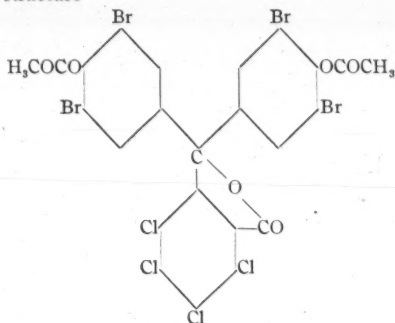
The diacetate dissolves in concentrated sulphuric acid

¹ THIS JOURNAL, 26, 121.

slowly with a yellowish red color exactly like that produced by the phthalein itself. It is also easily saponified by alcoholic caustic potash, less readily by boiling aqueous solutions of the alkalis. It is more readily soluble in alcohol, benzene, and glacial acetic acid than the phthalein itself.

The melting point of the pure product was found to be 190° – 191° .

As it is colorless and contains two acetyl groups it must have the structure

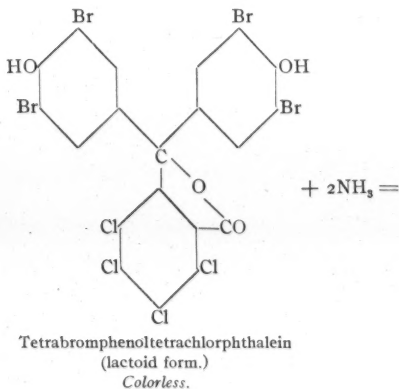


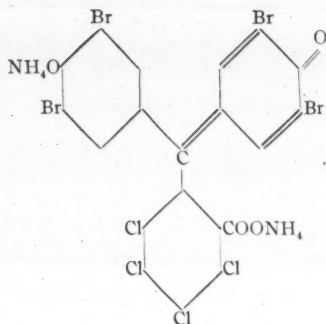
The Diammonium Salt of Tetrabromophenoltetrachlorophthalein.

—A weighed amount of the pure phthalein was placed in a platinum boat and introduced into an apparatus through which was passed ammonia gas dried over soda-lime. The phthalein immediately became colored dark blue, owing to the formation of the ammonium salt. At the end of two hours the boat containing the ammonium salt was removed from the apparatus and allowed to remain exposed to the air for two minutes to permit any excess of ammonia to escape. The boat was then placed in a weighing tube, the stopper inserted, and the increase in weight ascertained. The following result was obtained:

Weight of substance, gram.	Weight of salt, gram.	Weight of NH_3 absorbed, gram.	Ammonia, per cent.
0.4080	0.4272	0.0194	4.54
Calculated for $\text{C}_{20}\text{H}_4\text{Cl}_4\text{Br}_4\text{O}_4(\text{NH}_4)_2$,			4.23

The substance is therefore the diammonium salt. On allowing it to stand exposed to the air in a room free from acid fumes it gradually loses its deep blue color from the loss of ammonia, until it is finally white and returns to the original weight of the phthalein taken. Under these conditions, therefore, the phthalein yields a diammonium salt, which is unstable at ordinary temperatures in air free from ammonia. It is highly probable that this same salt is formed when the phthalein is dissolved in an excess of ammonia solution. When this solution is treated with excess of acid the phthalein is precipitated. Tetrabromphenoltetrachlorphthalein acts then as a dibasic acid, like tetrabromfluorescein or eosin, which forms a diammonium salt under the same conditions. It is very interesting to note that this transformation from the *colorless* phthalein to the *blue* diammonium salt and back again takes place here in the solid form as well as in solution. It is necessary therefore to assume that the change from the lactoid form to the quinoid and back again can also take place in *solids*. This change may be represented as follows:





Diammonium salt
(quinoid form.)

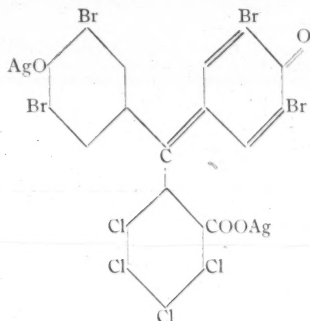
Blue.

The Disilver Salt of Tetrabromophenoltetrachlorophthalein.—

The disodium salt was first prepared by dissolving 7.72 grams of the phthalein in absolute alcohol and treating this solution with 0.46 gram of sodium in absolute alcohol. The solution was evaporated to dryness on the water bath and the blue disodium salt resulting dissolved in water. The solution was then filtered and a solution of silver nitrate added in excess. The silver salt was precipitated as a light blue gelatinous mass. This was filtered off on a Buchner funnel with suction, washed free from silver nitrate, and dried, first on a porous plate and then to constant weight in a vacuum desiccator over concentrated sulphuric acid. In the dried condition the silver salt has a blue color. To analyze it, a weighed quantity was placed in a Kjeldahl digestion flask and warmed on a sand bath with *aqua regia*. In this way oxidation was effected and all the silver bromide formed was converted into the chloride. After the oxidation was completed, the *aqua regia* was evaporated off and the silver chloride dissolved in ammonia to remove it from the flask and reprecipitated by adding nitric acid. It was then filtered off on a Gooch crucible, washed, dried, and weighed. The following are the results obtained:

	Weight of substance, gram.	Weight of silver chloride, gram.	Silver, per cent.
I.	0.5020	0.1450	21.74
II.	0.3134	0.0908	21.81
	Calculated for $C_{20}H_4Cl_4Br_4O_4Ag_2$		21.90

The substance is therefore the disilver salt and is to be represented by the formula



Ethers of Tetrabromphenoltetrachlorphthalein.

The Colorless Dimethyl Ether of Tetrabromphenoltetrachlorphthalein.—Tetrabromphenoltetrachlorphthalein (7.72 grams) was dissolved in absolute methyl alcohol in a flask connected with an upright condenser, and treated with a solution of 0.46 gram of sodium in absolute methyl alcohol. An excess of methyl iodide was then added and the contents of the flask were heated on the water bath to boiling. The colorless dimethyl ether which separated out after heating for a short time was filtered off from time to time as it accumulated. Sodium methylate in methyl alcohol and methyl iodide were added as the solution became decolorized, and the heating was continued for 72 hours. Seven and forty-five hundredths grams of the crude product, consisting almost entirely of the dimethyl ether, were obtained, a yield of 93 per cent of the calculated.

The product was crystallized from benzene after the mono-methyl ether, the ether ester, and any unchanged phthalein

had been removed by boiling with caustic soda solution.

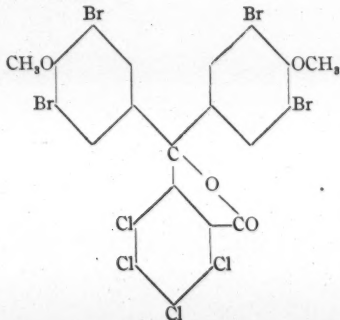
Analyses of the air-dried product by the indirect method with lime gave the following results:

	A. weight of substance, gram.	B. weight of silver halides, gram.	C. N/10 silver nitrate, cc.	Chlorine, per cent.	Bromine, per cent.
I.	0.1862	0.3085	18.60	17.52	40.34
II.	0.1663	0.2750	16.60	17.66	39.96
	Calculated for $C_{20}H_4Cl_4Br_4O_4(CH_3)_2$			17.73	39.99

The substance is therefore the dimethyl ether of tetrabrom-phenoltetrachlorophthalein. It is insoluble in dilute aqueous alkalis, but dissolves without color in alcoholic caustic potash on boiling, forming the potassium salt of the carbinolcarboxylic acid. The dimethyl ether is insoluble in cold concentrated sulphuric acid. It imparts not a trace of color to the acid and even when the mixture is heated to boiling the sulphuric acid takes on only a faint pink tint, which it loses on cooling. The basic properties of the phenolphthalein have been practically neutralized in this compound. The dimethyl ether is not very soluble in methyl or ethyl alcohols. It is soluble in ether, benzene, and glacial acetic acid. The pure product melts at 265° – 266° . The crystals from benzene were examined by Professor Gill, who reports as follows:

"The crystals form cloudy needles with high double refraction and oblique extinction. They are surely monoclinic or triclinic, probably the latter."

As the dimethyl ether is colorless, insoluble in aqueous alkalis, and not saponified by alcoholic caustic potash, it must have the structure



The Colorless Diethyl Ether of Tetrabromphenoltetrachlorophthalein.—The same method was used in preparing this ether as in making the dimethyl ether. The yield of the crude product, which consisted almost entirely of the diethyl ether, was 94 per cent of the calculated. As it is not very soluble in ethyl alcohol, it crystallized out as fast as formed, so that it was not acted on further by the sodium ethylate. This probably accounts for the fact that it was so easily obtained, while it was impossible to prepare a diethyl ether of phenoltetrachlorophthalein by the same method, as the sodium ethylate removed chlorine from the compound.

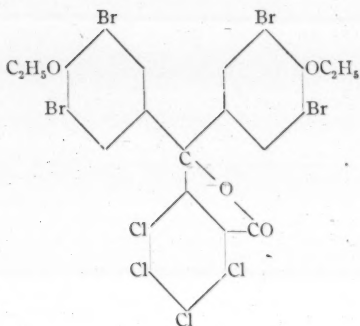
The diethyl ether, after treatment with caustic soda solution to remove unchanged phthalein, monoethyl ether, and the ether ester (by saponification), was recrystallized from benzene. On analysis of the air-dried material by the indirect method with lime the following results were obtained:

	A. weight of substance, gram.	B. weight of silver halides, gram.	C. N/10 silver nitrate, cc.	Chlorine, per cent.	Bromine, per cent.
I.	0.1942	0.3112	18.80	17.26	38.52
II.	0.1812	0.2906	17.55	17.18	38.63
	Calculated for $C_{20}H_4Cl_4Br_4O_4(C_2H_5)_2$,			17.13	38.64

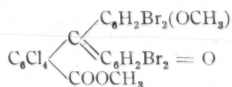
The product is therefore the diethyl ether of tetrabromphenoltetrachlorophthalein. It melts at 201° – 202° when perfectly pure, and is colorless. The crystals from benzene were examined by Professor Gill, who reports as follows:

"The long white needles are seen under the microscope to be partly clear and translucent, but mostly cloudy as though they had undergone a paramorphic change. The clear crystals have parallel extinction and medium interference colors. The long diameter is the direction of greater elasticity. They are probably orthorhombic; optically positive, with small optical angle and plane of optical axes at right angles to the long direction."

The properties of the diethyl ether are similar to those of the dimethyl ether, and its structural formula is represented as follows:



An attempt was made to prepare the colored, dimethyl ether ester of the tetrabromophenoltetrachlorophthalein,



by the direct action of dry methyl iodide on the dry dipotassium salt suspended in dry benzene, the method by which R. Meyer¹ succeeded in preparing a colored, diethyl ether ester of phenolphthalein. After heating for 20 hours on the boiling water bath no reaction had taken place. The dipotassium salt was therefore converted into the disilver salt, which, when dry, was suspended in dry benzene and heated with dry methyl iodide, the method which R. Meyer used to prepare the colored diethyl ether ester of tetrabromophenolphthalein (see page 353). Reaction took place slowly and the benzene solution took on a deep yellow color, showing the formation of the colored ether ester. After 10 hours' heating the benzene solution was filtered and evaporated to crystallization. Nothing but the colorless dimethyl ether melting at 265° could be isolated, however, and it is evident that, here, as in the case of the colored ether esters of phenolphthalein and of tetrabrom-

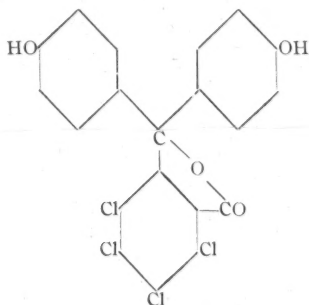
¹ Ber. d. chem. Ges., **40**, 3603 (1907), and **41**, 2446 (1908).

phenolphthalein made by R. Meyer, the colored dimethyl ether ester of tetrabromphenoltetrachlorphthalein is first formed and is then converted into the colorless dimethyl ether.

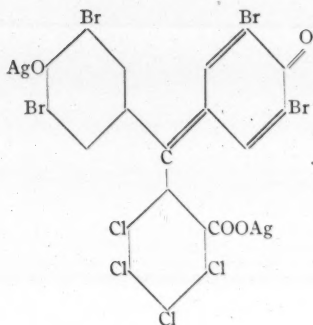
SUMMARY.

The more important facts brought out in this paper may be summed up as follows:

1. Phenoltetrachlorphthalein and tetrabromphenoltetrachlorphthalein, their diacetates, and dimethyl ethers have been prepared and analyzed. These are all colorless compounds and therefore probably have the lactoid structure,



2. Phenoltetrachlorphthalein, like phenolphthalein itself, is a weak acid, its red, alkali salts being decomposed by the carbon dioxide of the air. The tetrabromphenoltetrachlorphthalein is a stronger acid. We have prepared and analyzed its colored diammonium and disilver salts. The diammonium salt is unstable and gradually loses all of its ammonia on exposure to the air at ordinary temperatures. Both salts have a dark blue color and are therefore probably derived from the quinoid form of tetrabromphenoltetrachlorphthalein,



The transformation of the colorless lactoid form of tetrabromphenoltetrachlorphthalein into the colored quinoid diammonium salt, and back again, therefore takes place in the *solid* form as well as in solution.

3. The acidifying influence of the four chlorine atoms in phenoltetrachlorphthalein or of the four chlorine atoms and four bromine atoms in tetrabromphenoltetrachlorphthalein is not sufficient to make these substances strong enough acids to be used as indicators for titrating carbonates. They can, however, be used as indicators in the same way as phenolphthalein itself. Indeed, for titrating organic acids or alcoholic solutions, phenoltetrachlorphthalein is preferable to phenolphthalein.

4. Neither phenoltetrachlorphthalein nor tetrabromphenoltetrachlorphthalein form esters by the catalytic method with hydrochloric acid or by the method with sulphuric acid. This is in accord with the Victor Meyer rule that two substituents in the ortho position to the carboxyl group retard or altogether inhibit the formation of esters.

5. Unlike phenolphthalein, phenoltetrachlorphthalein and tetrabromphenoltetrachlorphthalein do not combine with stannic or aluminium chlorides to form double salts, nor do they combine with hydrochloric acid.

Further work on tetraiodophenoltetrachlorphthalein, tetra-

nitrophenoltetrachlorphthalein, and tetrachlorfluorescein is in progress in this laboratory.

CORNELL UNIVERSITY,
February, 1909.

[Contributions from the Chemical Laboratory of Cornell University.]

TETRACHLORPHTHALIC ACID.¹

BY T. G. DELBRIDGE.

In collaboration with Dr. W. R. Orndorff, the author has been engaged for the past three years in an investigation of tetrachlorgallein and some of its derivatives. The results of this research are soon to be published in *THIS JOURNAL*. In order to obtain pure tetrachlorgallein, it was necessary to start with pure tetrachlorphthalic anhydride. The study of methods of purifying tetrachlorphthalic acid led to the discovery of certain inaccuracies in the literature concerning this substance and the following paper is presented for the purpose of correcting these errors and of making some additions to our knowledge of tetrachlorphthalic acid.

HISTORICAL.

Tetrachlorphthalic acid was first prepared in 1868 by Graebe,² by oxidation of pentachloronaphthalene in a sealed tube at 180°–200° with nitric acid (1.15–1.20). The product thus obtained was purified by sublimation and by crystallization from water. It was dried at 100° and analyzed with the following results: 0.2525 gram gave 0.8826 gram CO₂ and 0.0198 gram H₂O; 0.2778 gram gave 0.5281 gram AgCl.

	Calculated for C ₆ H ₂ Cl ₄ O ₄ .	Found.
C	31.58	31.77
H	0.66	0.87
Cl	46.71	47.02

It is to be noted that the weight of carbon dioxide is incorrectly given; it must have been 0.2942 gram (one-third of the weight given above), if the carbon found was 31.77 per cent.

¹ Read at the Baltimore meeting of the American Chemical Society.

² *Ann. Chem. (Liebig)*, **149**, 18.

Graebe concludes from these analyses that the compound is tetrachlorphthalic acid and that it is a derivative of orthophthalic acid, since it resembles this compound in appearance and properties, especially in the formation of an anhydride. He states that the acid is easily soluble in hot water, slightly in cold. On rapid cooling of the hot saturated solution, colorless leaflets separate, while by slow crystallization, thick hard plates are obtained. The acid dissolves readily in alcohol and ether, melts at 250° , and changes, with loss of water, into the anhydride which melts at 245° . Analysis of the anhydride, prepared by sublimation, showed that it has the formula $C_6Cl_4O_3$, analogous to that of phthalic anhydride. In this paper Graebe describes very briefly the ammonium, lead, and silver salts of the acid, only the last being analyzed.

The preparation of tetrachlorphthalic acid in quantity by Graebe's method was of course impossible, since it involved the conversion of dichlornaphthoquinone into pentachlornaphthalene by the action of phosphorus pentachloride. In 1882, however, tetrachlorphthalic acid was prepared commercially by a process kept secret at first but covered by patent in 1885. This process consisted in the direct chlorination of phthalic anhydride in the presence of antimony pentachloride, the yield being almost quantitative. Thus it became possible for Graebe to make an extended study of the compound, and his second paper¹ on tetrachlorphthalic acid contains most of our knowledge of this compound up to the present time. According to this article, chlorination on the small scale by the factory method gave a mixture of tetrachlorphthalic acid and acids containing less chlorine. The pure tetrachlorphthalic acid was obtained from this mixture by crystallization from water. Chlorine, calculated for $C_6Cl_4(COOH)_2$, 46.71 per cent; found, 46.35 per cent. This acid proved to be identical in every respect with the one obtained by oxidation of pentachlornaphthalene and described in the first paper.² According to Graebe, the commercial acid is nearly pure, a direct chlorine determination giving 45.5 per cent, instead of

¹ Ann. Chem. (Liebig), **236**, 318.

² Loc. cit.

46.7 per cent, calculated. One crystallization of this product from water gave a perfectly pure acid, chlorine, 46.67 per cent. The properties of this acid agree with those reported in the first paper. The corrected melting point of the anhydride was found to be 252° , a short thermometer being used so that the mercury was entirely immersed in the bath. One hundred parts of water were found to dissolve 0.57 part of the acid at 14° and 3.02 parts at 99° . A large number of derivatives of the acid, including the potassium, barium, copper, and zinc salts, were prepared and studied by Graebe.

In 1886, the year before Graebe's second paper appeared, Claus and Wenzlik¹ oxidized β -heptachlornaphthalene with concentrated nitric acid (1.5) and obtained as one of the products tetrachlorphthalic acid. Purified by crystallization from water, it melted at 250° (uncor.) and gave on analysis:

	Calculated for $C_6Cl_4(COOH)_2$.	Found.
C	31.58	31.39
H	0.66	0.68
Cl	46.71	46.85

No additional information is given by these authors.

In 1892, Zincke and Günther² found that perchloroacetophenone-*o*-carboxylic acid was decomposed by dilute alkalis, yielding chloroform and tetrachlorphthalic acid. The acid, purified by crystallization from hot water, agreed in all its properties with the tetrachlorphthalic acid described by Graebe. It crystallized in white, glistening leaflets which melted at 249° – 250° with formation of bubbles. Allowed to harden and then heated again, the mass melted at 245° , which Graebe gives as the melting point of the anhydride. The acid was dried over sulphuric acid and analyzed:

	Calculated for $C_6Cl_4(COOH)_2$.	Found.
C	31.59	31.54
H	0.66	0.97
Cl	46.67	46.37

A number of other investigators have used tetrachlorphthalic acid in the preparation of other compounds, but as they

¹ Ber. d. chem. Ges., **19**, 1166.

² Ann. Chem. (Liebig), **272**, 266.

give no analyses of the acid itself, their work need not be considered here. The following table presents a summary of that work on tetrachlorophthalic acid with which the author is especially concerned:

Date Observer	1868 Graebe.	1886 Claus, Wenzlik.	1887 Graebe.	1892 Zincke, Günther.	-Calculated for $C_6Cl_4(COOH)_2$.
Acid dried	100°	?	?	H_2SO_4	
Carbon	31.77	31.39		31.54	31.59
Hydrogen	0.87	0.68		0.97	0.66
Chlorine	47.02	46.85	46.35	46.37	46.68
			46.67		
Melting point	250°	250°	250°	250°	
Crystal form	Leaflets		Leaflets	Leaflets	
	Plates		Plates		
Melting point of anhydride	245°		252° (cor.)	245°	

EXPERIMENTAL.

Determination of Chlorine.—A number of methods were tried at the beginning of the investigation. The sodium peroxide method of Pringsheim¹ was found to be unsatisfactory, as shown by the following analyses² of pure sublimed tetrachlorophthalic anhydride, dried at 180°:

Substance, gram.	Silver chloride, gram.	Chlorine, per cent.
0.5885	1.1715	49.26
0.5887	1.1638	48.92
0.5290	1.0491	49.07
0.5889	1.1783	49.51
0.4387	0.8861	49.98
	Calculated for $C_6Cl_4O_3$,	49.62

The next method tried was that described by Stepanow,³ who decomposes the substance by the action of sodium on its alcoholic solution. In an analysis made by this method, 0.3347 gram of pure tetrachlorophthalic anhydride required 8.71 cc. of tenth-normal silver nitrate solution. Chlorine found, 9.23 per cent; calculated, 49.62 per cent. In a recent

¹ Ber. d. chem. Ges., **36**, 4244; **38**, 2429; THIS JOURNAL, **31**, 386.

² International Atomic Weights for 1909 were used.

³ Ber. d. chem. Ges., **39**, 4056.

article,¹ C. W. Bacon recommends a modification of the Stepanow method, stating that "If the simple directions are followed, success may be confidently expected in every case." This expectation is not realized in the case of tetrachlorophthalic anhydride, as shown by the following analysis: 0.1572 gram of pure tetrachlorophthalic anhydride was dissolved in 24.5 cc. of alcohol (98.1 per cent) and 3.1 grams of sodium added in small portions over a period of forty-five minutes. The mixture was then boiled for one hour and Bacon's directions followed in detail. 5.37 cc. of tenth-normal silver nitrate solution were required. Chlorine found, 12.11 per cent; calculated, 49.62 per cent. The extremely low results obtained by the Stepanow method and by Bacon's modification confirm the statement of Graebe² that tetrachlorophthalic acid dissolved in 96 per cent alcohol is for the most part unacted upon by sodium amalgam.

The method of determining chlorine finally adopted was a modification of the lime method, combined with titration according to Volhard. The combustion with lime is made in a Jena glass tube and the contents are transferred to an Erlenmeyer flask and dissolved in dilute nitric acid in the usual way. An excess of tenth-normal silver nitrate solution is then added slowly from a burette³ and the flask closed with a rubber stopper and shaken vigorously for several minutes. The precipitate, consisting of carbon, silver chloride, and insoluble matter from the lime, is filtered off with suction on filter paper on a platinum cone and is washed thoroughly with dilute nitric acid. In the filtrate, which has a volume of 350-400 cc., the excess of silver nitrate is determined by titration with a tenth-normal solution of ammonium thiocyanate, ammonium ferric sulphate being used as indicator. The removal of silver chloride⁴ and carbon by one filtration does not lessen the

¹ J. Am. Chem. Soc., **31**, 49.

² Ann. Chem. (Liebig), **238**, 323.

³ The burettes used in this investigation were 25 cc. Schellbach burettes, 45 cm. long, graduated in 0.05 cc. and calibrated by the Herzogliches Sächsisches Eichamt, Gehlberg.

⁴ The silver chloride must be removed before titration with ammonium thiocyanate. Compare Sutton: Volumetric Analysis (1904), page 144; Morse: Exercises in Quantitative Analysis (1905), page 220; Rosanoff and Hill: J. Am. Chem. Soc., **29**, 269 (1907).

accuracy of the results, the same values being obtained by gravimetric determination in the usual way and by the volumetric method, both with and without separate filtration of carbon and silver chloride. During the past three years, the author has made more than a hundred chlorine determinations by this method and the results have been uniformly satisfactory.

The tetrachlorophthalic acid used in the early part of the investigation was obtained from Kahlbaum. It was nearly white, melted at 253° – 255° (cor.), and left no residue on ignition. On drying in a water oven at 98° , the loss of weight was so large and so continuous as to prove that the anhydride is volatile at this temperature. Chlorine in the Kahlbaum acid, as received, was determined by the ordinary lime method:

Substance, gram.	Silver chloride, gram.	Chlorine, per cent.
0.2160	0.4156	47.61
0.3098	0.5954	47.56
Calculated for the acid, $C_6Cl_4(COOH)_2$,		46.68
Calculated for the anhydride, $C_8Cl_4O_3$,		49.62

In order to prove that this product is really a mixture of tetrachlorophthalic acid and its anhydride, twenty grams of the substance were extracted repeatedly with boiling water, in which the anhydride is practically insoluble. The residue, when dried, weighed five grams and dissolved completely in boiling sodium carbonate solution, carbon dioxide being set free. On acidifying this solution, tetrachlorophthalic acid was precipitated. Hence Kahlbaum's acid contains about twenty-five per cent of the anhydride.

This Kahlbaum acid was crystallized from water and the resulting product dried to constant weight at 20° . On analysis for chlorine, 0.2163 gram of substance required 27.61 cc. of tenth-normal silver nitrate solution.

	Chlorine.
Found,	45.26
Calculated for $C_6Cl_4(COOH)_2$,	46.68
Calculated for $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$,	45.34
Calculated for $C_6Cl_4(COOH)_2 \cdot H_2O$,	44.07

This analysis indicated either that the compound was impure or else that it contained a half-molecule of water. The purity of the acid was checked by determining its molecular weight by titration¹ with standard alkali and phenolphthalein. A weighed portion of the compound was suspended in 100 cc. of water in a Jena flask, about 0.5 cc. less than the required amount of tenth-normal sodium hydroxide solution added, and the slightly acid solution boiled for one minute to expel carbon dioxide. The titration was finished after cooling to 50° and adding the phenolphthalein. The sodium hydroxide was titrated under the same conditions against hydrochloric acid standardized by the silver chloride method.

In order to check the method and reagents, titrations were made on pure succinic acid, dried at 70°. The results were as follows:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Molecular weight.
O. 1244	20.96	118.7
O. 1040	17.54	118.6
O. 1200	20.32	118.1
O. 1299	22.04	117.9
O. 1346	22.73	118.4
O. 1433	24.33	117.8
O. 1423	24.11	118.0
Calculated for $C_2H_4(COOH)_2$,		118.05

The results obtained by titration of the crystallized tetrachlorphthalic acid are as follows:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Molecular weight.
O. 3277	20.92	313.3
O. 3250	20.71	313.9
O. 3150	20.16	312.5
Calculated for $C_6Cl_4(COOH)_2$,		303.9
Calculated for $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$,		312.9
Calculated for $C_6Cl_4(COOH)_2 \cdot H_2O$,		321.9

Hence the titration, like the chlorine determination, indicates that the acid really contains a half molecule of water,

¹ It was later found that Jacobson also recommends this method for determining water of crystallization. Ber. d. chem. Ges., 15, 1854.

since the presence of any tri- or dichlorophthalic acid would lower the molecular weight.

An attempt was then made to drive off the half molecule of water by heating in an oven at 98° . The loss of weight was continuous, due to the volatility of the anhydride, amounting to 9.7 per cent in 118 hours, the calculated loss for the conversion of the acid, $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$, into the anhydride, $C_6Cl_4O_3$, being only 8.6 per cent. The product obtained in this experiment was insoluble in water and a chlorine determination showed that it was tetrachlorophthalic anhydride:

0.1640 gram of substance required 22.80 cc. of tenth-normal silver nitrate solution.

	Calculated for $C_6Cl_4O_3$	Found.
Cl	49.62	49.30

The crystallized acid is therefore converted into the anhydride, even at 98° , and at this temperature the anhydride is somewhat volatile.

The acid used in the latter part of the investigation was procured from the Fabriques de Produits Chimiques de Thann et de Mulhouse, Alsace, through the Heller & Merz Company, Newark, New Jersey. This acid was nearly white, melted at 252° – 254° (cor.), and contained less than two per cent of the anhydride. Titration of this acid with standard alkali by the method described gave for the molecular weight, 311.1 and 310.9; calculated for $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$, 312.9. Chlorine determinations on the acid, as received, gave the following results:

Substance, gram.	Tenth-normal silver nitrate, cc.	Chlorine, per cent.
0.1781	22.24	44.28
0.1793	22.43	44.36
Calculated for the acid with $\frac{1}{2}H_2O$,		45.34

Hence this acid is fairly pure. It is to be noted that Graebe¹ found 45.5 per cent of chlorine in the acid from this source.

This commercial tetrachlorophthalic acid was dissolved in acetone, in which it is excessively soluble, and the solution was

¹ Ann. Chem. (Liebig), **238**, 320.

decolorized with bone black, filtered, and poured into a large volume of water. Within a few minutes the acid began to crystallize in very thin leaflets which were filtered off, washed with cold water, and dried to constant weight at 20°. Chlorine determinations on this product gave the following results:

Substance, gram.	Tenth-normal silver nitrate, cc.	Chlorine, per cent.
0.1669	21.30	45.25
0.1701	21.70	45.24
Calculated for $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$,		45.34

The molecular weight of this acid was then determined by titration with tenth-normal sodium hydroxide solution. A decided improvement in the method already described¹ consists in the use of phenoltetrachlorophthalein² as the indicator. This compound has superseded phenolphthalein in the author's laboratory and is an indicator to be recommended very highly, possessing a real advantage over phenolphthalein in that it is somewhat less sensitive to carbon dioxide and that the end point is sharper. Using phenoltetrachlorophthalein as indicator, the following results were obtained on the crystallized tetrachlorophthalic acid:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Molecular weight.
0.3665	23.41	313.1
0.3702	23.64	313.2
0.3676	23.48	313.1
0.3742	23.89	313.3
0.3814	24.35	313.3
Calculated for $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$,		312.9
Calculated for $C_6Cl_4(COOH)_2$,		303.9

The close agreement of these results with each other is due largely to the use of phenoltetrachlorophthalein as indicator. It is evident that titration is more accurate than chlorine determination in testing the purity of the acid.

Further proof that the crystallized tetrachlorophthalic acid contains a half molecule of water was furnished by the deter-

¹ Page 399.

² Orndorff and Black: *THIS JOURNAL*, **41**, 349.

mination of carbon and hydrogen. The Dennstedt¹ method of combustion was abandoned after two failures to secure complete oxidation. The combustion was eventually made by burning in oxygen with de Roode's² mixture of lead chromate and lead oxide, a silver roll being used in place of the copper gauze. The difficulty of oxidizing the compound is shown by the failure of the Dennstedt method and by the fact that in one instance tetrachlorophthalic anhydride sublimed through a 10 cm. layer of hot lead chromate mixture. Analyses:

I. 0.3535 gram of substance gave 0.3979 gram of carbon dioxide and 0.0379 gram of water.

II. 0.3453 gram of substance gave 0.3869 gram of carbon dioxide and 0.0348 gram of water.

	Found.		Calculated for	Calculated for
	I.	II.	$C_6Cl_4(COOH)_2$	$C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$
C	30.69	30.55	31.59	30.68
H	1.19	1.12	0.66	0.97

The composition of the crystallized tetrachlorophthalic acid is therefore undoubtedly represented by the formula $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$, and not by the one found in the literature.

After several failures to dry the acid to constant weight in an oven heated to various temperatures, some of it was placed *in vacuo* with phosphorus pentoxide above and below.³ The loss was slow and uniform but much greater than that required for the loss of a half molecule of water. Drying was discontinued after 302 days, the loss in that time amounting to 6.4 per cent, while that calculated for the loss of a half molecule of water is only 2.9 per cent. This loss, together with the fact that most of the dried substance was insoluble in boiling water, shows that tetrachlorophthalic anhydride is formed at room temperature under these conditions.

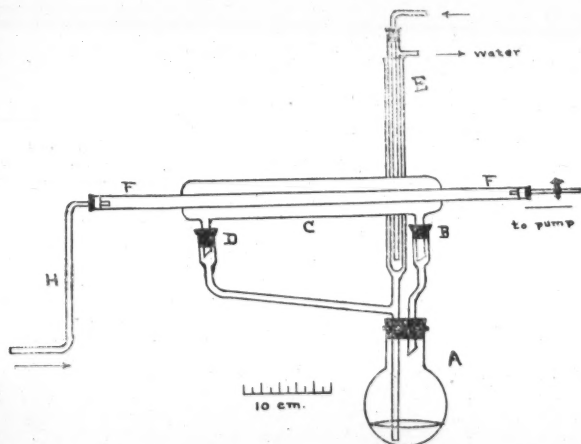
Although it was impossible to dry the crystallized acid to constant weight in an oven, it seemed likely that the rate of loss might give some indication as to the presence of the half

¹ Anleitung zur vereinfachten Elementaranalyse, Hamburg, 1906, S. 51.

² THIS JOURNAL, 12, 226.

³ This arrangement has been found extremely efficient in shortening the time required for drying.

molecule of water. The drying apparatus used for this purpose was one devised in connection with the study of easily oxidized derivatives of tetrachlorgallein. The idea is not a new one¹ but the utility and simplicity of the apparatus justifies a description of its essential features. The 500 cc. balloon flask (A) of Jena glass contains 150 cc. of some liquid of suitable boiling point. The vapors from the boiling liquid pass through the jacket of the condenser (C), inclined at a small angle, as shown, and are then returned to the flask,



loss being prevented by the Beckmann condenser (E). The condenser (C) is covered by a sheath of asbestos paper to prevent radiation, so that the inner tube (F) is heated uniformly to the temperature of the vapor surrounding it. The joints (B) and (D) are made with corks, as shown. The apparatus is supported on an iron stand by a clamp on the condenser (C) and by an asbestos ring under the flask (A). Substances are dried in boats which are pushed into the tube (F). One

¹ Compare Storch: *Ber. d. österr. Ges. Förd. chem. Ind.*, **15**, 13.

end of this tube is closed by a rubber stopper carrying a glass tube drawn out to a capillary at (H) and connected through purification apparatus to a suitable gas supply. The other end of the tube (F) is connected with a suction pump by means of which the air may be removed from the apparatus, while hydrogen, carbon dioxide, or other suitable gas is allowed to enter through (H). By properly adjusting the size of the capillary (H), it is possible to maintain a constant flow of gas through the tube (F) at a pressure of only twenty millimeters. The constriction (H) is omitted in drying at atmospheric pressure. If even boiling of the liquid is ensured by the addition of broken porcelain, the temperature in the tube (F) is constant and uniform, even at 200° (nitrobenzene). The construction of this apparatus presents no difficulty, all of the parts needed being regular laboratory equipment. Among its advantages are the following: Very little gas is required for heating; drying is exceedingly rapid, especially when the entering gas is dried with phosphorus pentoxide; there is no danger of contaminating the substance; most important of all is the fact that the outflowing gas may be easily examined, qualitatively and quantitatively, for volatilized ammonia, hydrochloric acid, benzene, acetone, etc. Condensation of moisture on the cold part of the tube (F) furnishes a simple method for the detection of water of crystallization.

Pure crystallized tetrachlorophthalic acid was dried in this apparatus at 109° (toluene), weighings being made at half-hour intervals. The rate of loss decreased uniformly until the twelfth hour when the weight became practically constant (0.2 milligram lost in one hour). The cold part of the drying tube was partly covered with a very thin film of volatilized anhydride, so that the observed loss is a trifle higher than the calculated.

Substance, gram.	Loss, gram.	Water, per cent.
0.4136	0.0365	8.82
0.4291	0.0378	8.81
Calculated for loss of $1\frac{1}{2}\text{H}_2\text{O}$ from $\text{C}_6\text{Cl}_4(\text{COOH})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$		8.64

The dried material was insoluble in boiling water and was further shown to be tetrachlorphthalic anhydride by its chlorine content. Found, 49.54 per cent; calculated, 49.62 per cent. Hence the crystallized acid is completely converted into tetrachlorphthalic anhydride at 109° with the loss of one and a half molecules of water, a further proof that the composition of the tetrachlorphthalic acid is represented by the formula $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$.

The crystallized acid corresponds in general to the description of Graebe.¹ It is slightly soluble in cold water, benzene, and chloroform, fairly soluble in hot water, alcohol and ether, while in acetone it is excessively soluble. Rapid cooling of the hot aqueous solution gave leaflets, slow crystallization by spontaneous evaporation at 20° gave thick plates. Slow cooling of the hot saturated solution in water gave fine needles, a form not mentioned by other investigators who have worked with this compound. The formation of these needlelike crystals is favored by the presence of a mineral acid.

Determination of the melting point of the acid gave results which do not agree with those obtained by previous investigators. All melting points given in this paper were taken with Anschütz² thermometers graduated in fifths of degrees and compared frequently with thermometers standardized by the Physikalisch-technisches Reichsanstalt. The thread of the mercury was entirely immersed in the sulphuric acid in every case and the observed melting point is therefore the corrected one. The apparatus used was that described by Thiele.³ This simple device is a valuable addition to laboratory equipment and deserves general recognition. The only objection to its use lies in the fact that poorly annealed tubes crack when heated. For this reason the author uses a quartz tube obtained from Heraeus. The Thiele apparatus made of Jena glass is in general use in this laboratory and is very satisfactory. Using this apparatus, it was found that tetrachlorphthalic acid, heated in a capillary tube, began to melt at 255° and was not completely melted until 257° . Contrary to the

¹ *Loc. cit.*

² Destillation unter vermindertem Druck, Bonn, 1887, S. 16.

³ Ber. d. chem. Ges., 40, 996.

statement of Graebe, no loss of water was noted. When allowed to solidify and then heated again, the substance melted at the same temperature as before. Graebe¹ found that the acid melted at 250° (uncor.) with loss of water and formation of the anhydride which melted at 245° (uncor.) or 252° (cor.). Having already proven that tetrachlorophthalic acid is readily converted into the anhydride, even at 98°, the author suspected that the observed melting point was not that of the acid but of its anhydride. To verify this view, pure anhydride was prepared, first by drying the acid at 105°, secondly by sublimation of this product. The anhydride prepared in both these ways melted at 255°–257° (cor.) and melted at the same temperature when heated a second time. The melting point interval seems to be large for a pure compound but the same results were obtained with products repeatedly crystallized from different solvents. In order to determine more exactly the true melting point of the substance, it was heated for 35 minutes at 254°.2 in a sulphuric acid bath surrounded by the vapor of boiling diphenyl. No melting could be observed and the temperature was raised by adding a little diphenylamine to the boiling diphenyl. The compound was completely melted after five minutes' heating at 254°.8–255°.2 (cor.). The correct melting point of tetrachlorophthalic anhydride is therefore very close to 255°, and the melting point of the acid is not noted since it goes over into the anhydride at fairly low temperatures.

A number of attempts were next made to obtain the anhydrous acid. Pure crystallized tetrachlorophthalic acid was dissolved in boiling water and this solution allowed to cool very gradually. The acid crystallized in long, thin plates which were dried to constant weight at 20° and titrated with standard alkali:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Molecular weight.
0.3638	23.24	313.1
0.3620	23.13	313.0
0.3590	22.95	312.9
Calculated for $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$,		312.9

¹ Loc. cit.

Determination of chlorine in this product confirms the above formula:

0.1769 gram of substance required 22.57 cc. of tenth-normal silver nitrate solution.

	Calculated for $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$.	Found.
Cl	45.34	45.24

The melting point of this acid was 255° – 257° (cor.) and its other properties were identical with those of the acid obtained by crystallization from very dilute acetone.

A solution of pure tetrachlorophthalic acid in water was allowed to stand for several weeks at 20° . At the end of this time a considerable amount of thick, transparent plates had crystallized out. They were separated from the solution, dried to constant weight at 20° , and titrated:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Molecular weight.
0.3612	23.06	313.3
0.3635	23.24	312.8
Calculated for $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$,		312.9

These crystals melted at 255° – 257° and had the other properties of the acid already described.

Pure tetrachlorophthalic acid was dissolved in water and the solution concentrated at the boiling point until a considerable amount of the acid had crystallized out. The solution was decanted at once, the crystals washed with a little hot water, and dried to constant weight at 20° . Titration with alkali showed that this acid also contained the half molecule of water:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Molecular weight.
0.3647	23.30	313.0
0.3578	22.88	312.8
Calculated for $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$,		312.9

As was stated before, fine needles are obtained when the hot saturated solution in water is allowed to cool fairly rapidly. These needles melt at the same temperature as the acid crys-

tallized in other ways and give the same molecular weight on titration:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Molecular weight.
0.3842	24.57	312.7
0.3847	24.59	312.9
Calculated for $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$,		312.9

Some of the pure acid was crystallized from anhydrous ether. The resulting crystals were extremely fine needles, melting at 255° – 257° (cor.) and still containing the half molecule of water, as shown by the following determinations:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Molecular weight.
0.3812	24.34	313.1
0.3824	24.46	312.7
Calculated for $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$,		312.9

Crystallized tetrachlorophthalic acid was boiled with 700 cc. of dry benzene, the benzene solution filtered from some undissolved acid, concentrated to 125 cc., and let stand overnight. The mass of slender prisms which separated was filtered off and allowed to dry. An attempt to titrate this product showed that it was insoluble in boiling water, a fact which indicated that it was the anhydride. Solution was finally effected by boiling for two to three hours with a large excess of standard alkali. The solution was then made slightly acid with tenth-normal hydrochloric acid, boiled to remove carbon dioxide, and titrated with sodium hydroxide, phenol-tetrachlorophthalein being used as indicator:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Molecular weight.
0.3743	26.18	286
0.4626	32.22	287
Calculated for $C_6Cl_4O_3$,		286

Further proof that the compound crystallized from benzene is really tetrachlorophthalic anhydride is furnished by its chlorine content. Chlorine calculated for $C_6Cl_4O_3$, 49.62 per cent; found, 49.53 and 49.45 per cent.

An attempt to crystallize the acid from benzene without distilling off any of the solvent, gave a product which also contained some anhydride detected by its insolubility both in boiling water and dilute alkali. Crystallization from dry chloroform likewise gave a mixture of the acid and its anhydride, as shown by determination of its molecular weight by the method used in titrating the anhydride obtained by crystallization from benzene. 0.3141 gram of substance required 21.32 cc. of tenth-normal sodium hydroxide. Molecular weight, 295. These experiments give still further proof of the great ease with which tetrachlorophthalic acid is converted into tetrachlorophthalic anhydride.

Pure tetrachlorophthalic acid was crystallized from absolute methyl alcohol. The air-dried product melted at 254°–256° and contained some monomethyl ester, as shown by titration:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Combining equivalent.
0.3665	22.27	164.6
0.3757	22.43	167.5
Calculated for $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$,		156.4
Calculated for $C_6Cl_4 \begin{matrix} \diagup COOH \\ \diagdown COOCH_3 \end{matrix}$,		317.9

A second crystallization from methyl alcohol gave a mixture containing still more of the monomethyl ester. This product melted at 135°–140°, became solid again on further heating, and then melted at 255°–257°. V. Meyer and Sudborough¹ state that the melting point of pure monomethyl ester of tetrachlorophthalic acid is 142°, the substance becoming solid on further heating, and yielding tetrachlorophthalic anhydride which melts at 250°, according to these authors. The presence of methyl ester was further proved by titration: 0.3084 gram of substance required 11.40 cc. of tenth-normal sodium hydroxide; combining equivalent, found 270.5; calculated for the acid, 156.4; for its monomethyl ester, 315.9. Crystallization from alcohols was therefore abandoned.

¹ Ber. d. chem. Ges., 27, 3149.

Solutions of tetrachlorophthalic acid in dry acetone gave, on standing, large transparent crystals which lost acetone on exposure to air, soon crumbling to a white powder. This powder was allowed to stand until it had no odor of acetone, being stirred from time to time. Titration then showed that the compound contained the half molecule of water. More crystals from acetone were prepared, dried rapidly with filter paper, and weighed at once in a stoppered bottle. A slow current of air, dried with calcium chloride, was passed through the bottle until the weight became constant. The loss was 29.3 per cent; calculated for two molecules of acetone, 27.6 per cent.¹ The resulting product was white, melted at 255°–257°, and possessed the other properties of the acid with a half molecule of water. Titration, however, showed that this compound was the long-sought *anhydrous* acid:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Molecular weight.
0.3662	24.10	303.9
0.3656	24.04	304.2
0.3693	24.31	303.8
0.3722	24.49	304.0
Calculated for $C_6Cl_4(COOH)_2$,		303.9

In order to prove that this compound was really the anhydrous acid, some of it was converted into tetrachlorophthalic anhydride by drying at 109° in the apparatus already described. The same thin film of volatilized anhydride was formed on the cold part of the tube, as was observed in drying the acid containing a half molecule of water.²

0.8220 gram of substance lost 0.0500 gram.

	Calculated for conversion of $C_6Cl_4(COOH)_2$ into $C_6Cl_4O_3$.	Found.
Water	5.93	6.08

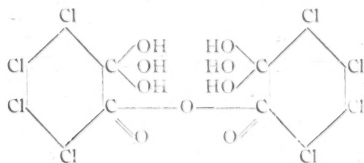
The anhydrous acid is unstable, taking up water from the air with the formation of the acid containing a half molecule of water, which was also obtained directly by leaving the

¹ The simultaneous loss of two molecules of acetone and a half molecule of water would amount to 29.2 per cent.

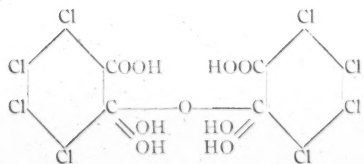
² Page 404.

acetone compound in the air of the laboratory. This fact, together with repeated failure to obtain the anhydrous acid by crystallization, leads the author to conclude that the *anhydrous* tetrachlorphthalic acid has never been prepared before. The results of the analyses given in the literature¹ can be easily explained on the assumption that previous investigators dried the acid and hence analyzed a mixture of tetrachlorphthalic anhydride and tetrachlorphthalic acid containing the half molecule of water.

It follows, therefore, from the experimental data presented that tetrachlorphthalic acid obtained by crystallization has the composition represented by the formula $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$, or better, $(C_8H_2O_4Cl_4)_2 \cdot H_2O$. The structural formula of the acid is probably



or possibly



Proof of either formula is not available at present.

An attempt was made to determine the molecular weight of the compound by the boiling point method. The solubility in chloroform, benzene, and water is too low. Determinations were made with ether and also with acetone before it was learned that the acid forms a compound with acetone.

Although no weight can be given to these results with our

¹ Tabulated on page 396.

present knowledge of the state of solution, the data obtained are given below:

Solvent.	Substance, gram.	Solvent, grams.	Rise.	Constant.	Molecular weight.
Ether	0.733	23.3	0°.205	21.1	324
Ether	0.691	28.8	0°.150	21.1	337
Acetone	0.967	31.5	0°.235	17.1	223
Acetone	0.691	26.8	0°.210	17.1	210
Water	0.850	45.3	0°.033	5.2	296

In order to test the correctness of the accepted formula for *phthalic acid*, the author made titrations on this compound, using phenoltetrachlorphthalein as indicator:

Substance, gram.	Tenth-normal sodium hydroxide, cc.	Molecular weight.
0.1965	23.69	165.9
0.1925	23.17	166.2
0.1948	23.47	166.0
Calculated for $C_6H_4(COOH)_2$,		166.05

These results not only prove the correctness of the usual formula for *phthalic acid*, but also indicate the accuracy of this method of analysis.

Crystals of tetrachlorphthalic acid obtained in various ways were examined by Professor A. C. Gill, of the Mineralogical Department of the University, and he makes the following report:

"As is the case with *phthalic acid*, slight differences in the conditions of crystallization of this substance produce marked variations in the habitus of the resultant crystals. Though these reach a diameter of about two mm., it has not as yet been possible to obtain accurate measurements of them. There is little doubt, however, that the substance is monoclinic. It very likely belongs to the dogmatic class, since it was frequently observed that the two prismatic faces on either side of the plane of symmetry were much striated, while their parallels gave fairly clear reflection images.

"The commonest shape is that of thin hexagonal or rhombic tablets. The rhombic plates show a plane angle of 47°, and those of hexagonal shape have this angle truncated by faces of the ortho-zone which may either be very small, or, in some

cases, much larger than the prismatic faces which produce the rhombic shape. These crystals are optically biaxial, positive, with strong double refraction, and the clinopinacoid as the optical axial plane. An obtuse bisectrix stands nearly normal to the tabular face. Extinction is parallel to the trace of the ortho-zone faces.

"Slow growth in water solution produced stout crystals of rhombohedral appearance bounded by four prismatic faces and a basal pinacoid. On some of these an ortho-dome was so largely developed as to produce an *octahedral* habitus."

The purification of very impure tetrachlorophthalic acid was next studied. A mixture was prepared containing 75 per cent tetrachlorophthalic acid, melting at 252° – 254° , and 25 per cent commercial dichlorophthalic acid, which melted at 105° – 135° . The melting point of the mixture was 220° – 240° . Purification was carried out as follows:

A. Fifty grams of this mixture were crystallized from 1500 cc. of water, bone black being used to decolorize the solution. The product, which was yellow, weighed 22 grams when dried at 20° , and melted at 251° – 254° (cor.).

B. The substance obtained in A was recrystallized from 800 cc. of water. The yellow product dried at 20° weighed 17 grams and melted at 254 – 256° (cor.).

C. Fifty grams of the original mixture were dissolved in 150 cc. of acetone, the solution filtered, poured into 1200 cc. of water, and let stand for three hours. The crystals which separated were filtered off and dried at 20° . Yield: 23 grams of a white product melting at 251° – 255° (cor.).

D. Fifty grams of the original mixture were boiled with 350 cc. of water containing 15 grams of sodium hydroxide and the solution filtered and again heated to boiling. An excess of hydrochloric acid, 1.10, was added very slowly, the solution being kept boiling vigorously by passing steam into it. Boiling in this way was continued for ten minutes and the solution filtered from the precipitated acid while hot. This acid was washed once with boiling water, then with cold water until free from chloride, and dried at 20° . This product was perfectly white, weighed 31 grams, and melted at 249° –

254°. The hot filtrates gave a crop of yellow crystals weighing 5.5 grams when dry.

The purity of these products was determined by the titration method described and the results, together with the melting points and percentage yield, are given in the following table:

	Substance, gram.	Tenth-normal sodium hydroxide, cc.	Mol. wt.	M. P.	Yield, per cent.
A.	0.3653	23.43	311.8	251°-254°	59.
	0.3650	23.43	311.6		...
B.	0.3825	24.46	312.8	254°-256°	45.
	0.3815	24.38	313.0		...
C.	0.3831	24.55	312.1	251°-255°	61.
	0.3589	23.00	312.1		...
D.	0.3773	24.35	309.9	249°-254°	83.
	0.3813	24.62	309.8		...
	Pure acid,		312.9	255°-257°	...

The purification of tetrachlorophthalic acid is therefore easily accomplished, the melting point is a reliable criterion of purity, and titration affords an easy way of checking the purity of the acid.

The following method of purifying the commercial acid gives perfect satisfaction: Boil 300 grams of this acid with two liters of water containing 45 grams of sodium hydroxide and filter the hot solution with suction on an 18 cm. Buchner funnel with a hardened filter. Heat the filtrate to boiling in a five-liter balloon flask by passing steam into it. Add gradually in the course of five minutes, 200 cc. of hydrochloric acid, 1.10, keeping the mixture boiling vigorously. Continue the boiling for thirty minutes longer and filter at once through an 18 cm. Buchner funnel with hardened filter, using strong suction. Transfer the precipitate to the balloon flask with 200 cc. of water, add 10 cc. of concentrated hydrochloric acid, and boil with steam for ten minutes. Filter at once as before, wash the precipitate with very cold water until it is free from chloride, and dry to constant weight at 20°. The product, which should be perfectly white, is pure tetrachlorophthalic acid, $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$. The yield is 240-260 grams,

about 80 per cent of the commercial acid used. The hot filtrates yield, on cooling, about 30 grams of a fairly pure acid which may be further purified as described, giving a total yield of about 90 per cent.

Tetrachlorophthalic Anhydride.

Tetrachlorophthalic acid may be converted into tetrachlorophthalic anhydride in a number of ways, as shown in the preceding pages. The anhydride has the composition represented by the formula $C_6Cl_4O_3$, as given by Graebe.¹ The substance used in analysis I., below, was obtained by drying tetrachlorophthalic acid, $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$, at 109°. Analysis II. was made on sublimed anhydride. Tetrachlorophthalic anhydride, obtained by crystallizing the acid from dry benzene, as already described,² was analyzed by Mr. C. K. Ou and his results are given in III. and IV.

	Substance, gram.	Tenth-normal silver nitrate, cc.	Chlorine, per cent.
I.	0.1618	22.61	49.55
II.	0.1610	22.49	49.53
III.	0.2130	29.75	49.53
IV.	0.2651	36.97	49.45
	Calculated for $C_6Cl_4O_3$,		49.62

The melting point of pure tetrachlorophthalic anhydride is 255°–257° (cor.) and not 252° (cor.), as given by Graebe. It is practically insoluble in boiling water and is dissolved very slowly by boiling tenth-normal sodium hydroxide.

The sublimed tetrachlorophthalic anhydride was submitted to Dr. Gill, who makes the following report:

"The somewhat flattened colorless needles reach a length of five or six mm., but are not more than 0.3 mm. in maximum transverse diameter. No measurements of end faces could be obtained. The following data, however, indicate beyond reasonable doubt that the substance occurs in monoclinic crystals, elongated in the direction of the ortho-axis. The three pairs of faces which are most prominent in the zone

¹ Ann. Chem. (Liebig), 149, 20.

² Page 408.

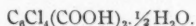
of elongation gave on the reflecting goniometer the following mean angles of mutual inclination: $46^{\circ}52'$, $41^{\circ}53'$, and $91^{\circ}15'$. Extinction is parallel in all positions of the needles when mounted in wax and rotated around their long axes between crossed Nicol prisms. Double refraction is strong. The plane of the optical axes is the clinopinacoid, *i. e.*, across the needles, and the bisectrix of a large optical angle (probably obtuse) emerges somewhat inclined from normal to the plane of flattening. If this angle, which was not measured, is obtuse, the substance is optically negative."

SUMMARY.

The more important facts brought out in this paper may be found in the following summary:

1. Tetrachlorphthalic acid crystallized from water under various conditions has the composition represented by the formula $C_6Cl_4(COOH)_2 \cdot \frac{1}{2}H_2O$, as shown (a) by determination of carbon, hydrogen, and chlorine; (b) by determination of the molecular weight of the acid by titration with sodium hydroxide; (c) by the weight lost in the conversion of the acid into its anhydride.
2. Tetrachlorphthalic acid with the half molecule of water may be crystallized from anhydrous ether without change.
3. Tetrachlorphthalic acid is very easily converted into its anhydride, $C_6Cl_4O_3$, this conversion having been brought about (a) by sublimation; (b) by drying at 98° ; (c) by crystallization from a benzene solution concentrated by distillation; (d) by drying for a long time *in vacuo* with phosphorus pentoxide.
4. The correct melting point of tetrachlorphthalic anhydride is 255° – 257° . The acid, when heated in a melting point tube, is converted into the anhydride and hence the melting point observed is the same as that of the anhydride.
5. Crystallization of tetrachlorphthalic acid from acetone gave a compound containing two molecules of acetone. When this compound is placed in a current of dry air at room temperature, it loses all its acetone and forms the *anhydrous*

tetrachlorophthalic acid, $C_6Cl_4(COOH)_2$. This anhydrous acid takes up moisture from the air, giving the stable acid



6. A simple apparatus is described for drying substances in a current of an indifferent gas at temperatures up to 200° and at low pressure if desired. This apparatus also permits the collection and examination of substances volatilized during drying.

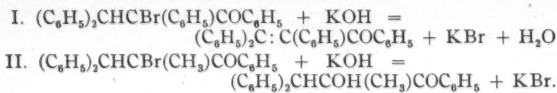
In conclusion, the author desires to acknowledge his indebtedness to Professor A. C. Gill for the description of crystals and especially to Professor W. R. Orndorff for valuable advice throughout the investigation. The study of tetrachlorophthalic acid is being continued and another paper will appear at an early date.

CORNELL UNIVERSITY.
March 6, 1909.

THE ACTION OF ALKALINE HYDROXIDES ON α -BROMKETONES.

By E. P. KOHLER.

In the course of some work on unsaturated ketones, I had occasion to study the reaction between potassium hydroxide and certain α -bromketones that, for the most part, may be regarded as derivatives of α -brompropiofenone. I found that the result of the reaction depends to an unusual degree upon the number, character, and location of the hydrocarbon residues contained in the ketone. The two typical reactions are represented by the equations:



The unsaturated ketones formed according to the first equation are not affected by potassium hydroxide, but α -oxyketones are exceedingly sensitive to alkaline reagents, hence the occurrence of the second reaction was, in some cases,

inferred from the nature of the secondary products that were obtained.

The behavior of a number of α -bromketones is shown in the following table, which gives only the percentage of unsaturated ketone, the remainder of the product being composed either of oxyketones or of substances formed from these by secondary reactions:

	Per cent.
$(C_6H_5)_2CHCBr(C_6H_5)COC_6H_5$ ¹	100
$(C_6H_5)(C_2H_5)CHCBr(C_6H_5)COC_6H_5$ ²	1-2
$(C_6H_5)_2CHCHBrCOC_6H_5$ ³	35-40
$(C_6H_5)_2CHCHBrCOC_6H_5OCH_3$ ⁴	35-40
$(C_6H_5)_2CHCHBrCOC(CH_3)_2$ ⁵	95
$(C_6H_5)_2CHC(CH_3)BrCOC_6H_5$ ⁶	none
$(C_6H_5)(C_2H_5)CHCHBrCOC_6H_5$ ⁷	none

From the behavior of these substances I concluded that this reaction does not give an unsaturated ketone unless the bromketone contains 2 aryl groups in the β position.

At a meeting of the *Gesellschaft deutscher Naturforscher und Aerzte*, held in 1906, Klages announced that he had obtained phenylvinyl ketone by treating brompropionylbenzene with potassium hydroxide. The report of the meeting does not state whether the α - or β -brom substitution product was used, but in a paper read before the Chemical Society at Heidelberg in 1908, Klages⁸ stated that phenylvinyl ketone and its homologues are easily obtained by the action of potassium hydroxide on α -brom derivatives of the corresponding saturated ketones. The products are described as intensely yellow, mobile liquids that boil without decomposition.

Klages presented no evidence that these yellow liquids are really unsaturated ketones. The only reaction discussed by him is that with organic magnesium compounds. He found that, "contrary to expectation," the substances reacted with two molecules of alkylmagnesium halides, one combining with the carbonyl, the other with the ethylene group. The resulting magnesium derivative, when decomposed with water,

¹ THIS JOURNAL, 38, 559.

² *Ibid.*, 38, 399.

³ *Ibid.*, 31, 652.

⁴ *Ibid.*, 38, 541.

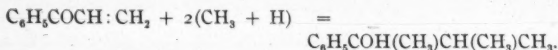
⁵ *Ibid.*, 38, 549.

⁶ *Ibid.*, 38, 552.

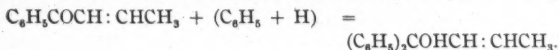
⁷ *Ibid.*, 38, 537.

⁸ Report by Klages: Chem. Ztg., 1908, p. 318.

gave a saturated tertiary alcohol with an alkyl group in the α position. The reaction between phenylvinyl ketone and methylmagnesium iodide, for example, is represented by the equation:



With phenylmagnesium bromide Klages obtained a reaction that he considers "normal"—addition of one molecule of the magnesium compound to form a derivative of an unsaturated alcohol. Thus with phenylpropenyl ketone:



As evidence in favor of this interpretation Klages states that the product loses water when heated with oxalic acid, and passes into a hydrocarbon boiling at 297° —"one of the few allene derivatives of which the constitution is known with certainty."

These results are at variance with those obtained with all other unsaturated ketones. If correct, they would mean that the physical and chemical properties of these unsaturated ketones are entirely different from those of substances so closely related to them as crotonic aldehyde,¹ acetacetone,² chloralacetophenone,³ mesityl oxide,⁴ and benzalacetophenone.⁵ They would mean, also, that organic magnesium compounds are capable of combining directly with the ethylene group, a process that it has not been possible to carry out with any other class of unsaturated compounds. For these reasons I thought it desirable to repeat the experiments of Klages. I have found, as expected, that he had no unsaturated ketones.

The reaction between potassium hydroxide and α -bromopropionylbenzene gave a mixture from which it was comparatively easy to separate a fraction boiling fairly constantly

¹ Ber. d. chem. Ges., **41**, 3200.

² THIS JOURNAL, **38**, 526.

³ *Ibid.*, **38**, 548.

⁴ *Ibid.*, **38**, 528.

⁵ *Ibid.*, **38**, 548.

between 217° and 219° —which Klages gives as the boiling point of phenylvinyl ketone. The composition of the yellow liquid, however, did not agree with that calculated for this substance. As different preparations invariably gave different analytical results, it was evident that the liquid contained substances extremely difficult, if not impossible, to separate by distillation. I therefore tried the reaction with the parabrom derivative of α -brompropionylbenzene in the hope of getting solid products. This ketone likewise gave a yellow liquid that boiled almost at a constant temperature under diminished pressure, but by repeated fractional distillations it was possible to separate a fraction that partially solidified in a freezing mixture. The bright yellow solid was found to be *p*-bromphenylmethyl diketone, $\text{BrC}_6\text{H}_4\text{COCOCH}_3$.

As this is a methyl ketone it was easy to remove it completely by digesting the mixture with acid sulphite. By further distillation, the residue was finally separated into *p*-brompropiphenone and *p*-brombenzoylmethylcarbinol:



By a similar procedure it was possible to prove that the liquid that Klages regarded as phenylvinyl ketone was, in reality, a mixture of methylphenyl diketone boiling at 217° – 219° , propiophenone boiling at 220° – 221° , and benzoylmethylcarbinol which distils with the others but decomposes when heated by itself.

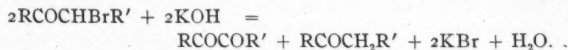
No unsaturated ketones could be detected among the products of the reactions described and none was obtained by the action of potassium hydroxide on α -bromisobutyl-*p*-bromphenyl ketone,



As this ketone has a tertiary hydrogen atom in the β position, it would be expected to lose hydrobromic acid as readily as any ketone of this type, but it gives only products analogous to those obtained with α -brompropionylbenzene. It may be asserted with considerable confidence, therefore, that unsaturated ketones of the type of benzoylethylene cannot be made by the action of alkaline hydroxides on α -bromke-

tones. The substances that Klages obtained by treating his yellow liquids with organic magnesium compounds are not derived from unsaturated ketones and his interpretation of this reaction is erroneous.

The diketones obtained by the action of potassium hydroxide on α -bromketones are formed in accordance with the equation



The relation between the amounts of mono- and diketone obtained is constant but the total yield of these products varies greatly because it depends upon conditions that are hard to control. By adding a dilute alcoholic solution of potassium hydroxide sufficiently slowly to a solution of the bromketone, it is possible to get 95 per cent of the calculated amount of the corresponding hydroxyl compound. The result is the same when a stronger solution is added rapidly to a boiling solution of the ketone, because, at this temperature, the replacement of bromine with hydroxyl is almost instantaneous. The diketone is formed in quantity only when the solution is alkaline; but as α -diketones are sensitive to bases, much of the product may undergo condensation to quinone, or hydrolysis to acid and aldehyde unless the concentration of the base is small and the temperature low.

Pure α -oxyketones are easily obtained by treating the brom compounds with anhydrous potassium acetate, and saponifying the acetates by boiling with water and barium carbonate. As treatment with potassium hydroxide, under the conditions most favorable for the formation of diketones from bromketones, gives neither diketones nor their condensation products it seems unlikely that the oxyketones are intermediate products in the reaction under consideration.

EXPERIMENTAL PART.

1. Experiments with α -Brompropio-*p*-bromphenone.

This ketone was obtained from brombenzene and α -brompropio-phenone by the Friedel and Crafts reaction. By using

carbon disulphide as a medium, and excess of active aluminium chloride, and exposing to sunlight to complete the reaction, it was possible to get approximately 95 per cent of the calculated amount of the pure ketone. With dry gasoline as a medium the amount of crude product was almost the same, but the loss in purifying was much greater so that the yield of pure ketone did not exceed 85 per cent.

Reaction with Potassium Hydroxide.—A solution obtained by dissolving potassium hydroxide in its own weight of water and diluting with 3 volumes of absolute alcohol was added, in portions of 10 cc., to a solution of 200 grams of the bromketone in the smallest possible quantity of cold absolute alcohol. The liquid was shaken vigorously, after each addition, until the temporary orange color disappeared, and the addition of hydroxide was stopped when this color persisted after shaking for 5 minutes. This required almost exactly one molecule of potassium hydroxide for one of ketone.

The liquid was acidified with acetic acid and distilled to remove most of the alcohol. The residue was then poured into water, the yellow oil dissolved in ether, washed with sodium carbonate, dried with fused sodium sulphate, and fractionated under diminished pressure.

The washings yielded 4.8 grams of an acid that after purification from alcohol melted at 251° . Analysis:

0.1769 gram substance gave 0.2700 gram CO_2 and 0.0414 gram H_2O .

	Calculated for $\text{C}_7\text{H}_5\text{O}_2\text{Br}$.	Found.
C	41.7	41.6
H	2.5	2.6

Analysis and melting point indicated that the substance was *p*-brombenzoic acid and this was confirmed by making the methyl ester, which melted at 74° .

The distillation under diminished pressure gave 102 grams of yellow distillate below 180° —the temperature at which the residue began to decompose with formation of water and rapid evolution of gas. The distillate, on cooling, deposited some more *p*-brombenzoic acid which was evidently formed

during the distillation. When this was removed the entire liquid distilled between 158° – 162° . After repeated distillations the last fraction solidified in a freezing mixture. The solid was separated by reverse filtration and crystallized from ligroin. Analysis:

I. 0.1635 gram substance gave 0.2870 gram CO_2 and 0.0465 gram H_2O .

II. 0.2133 gram substance gave 0.3746 gram CO_2 and 0.0614 gram H_2O .

	Calculated for $\text{C}_9\text{H}_7\text{O}_2\text{Br}$.	I.	Found.	II.
C	47.57	47.9		47.9
H	3.10	3.1		3.2

The molecular weight was determined in benzene ($K = 50$).

Solvent, grams.	Substance, gram.	Depression of freezing-point.	Molecular weight.
11.9	0.2595	0.505	216
11.9	0.4105	0.800	216
11.9	0.5605	1.076	220
	Calculated for $\text{C}_9\text{H}_7\text{O}_2\text{Br}$,		227

When the substance was boiled for two hours with an alcoholic solution of hydroxylamine it formed a sparingly soluble dioxime that separated from the hot solution in small lustrous prisms melting at 237° . As it is sparingly soluble in alcohol and ether it was purified by recrystallization from amyl alcohol. Analysis:

I. 0.2241 gram substance gave 0.3476 gram CO_2 and 0.0716 gram H_2O .

II. 0.4180 gram substance gave 41.2 cc. nitrogen at 20° and 754 mm.

	Calculated for $\text{C}_9\text{H}_9\text{O}_2\text{N}_2\text{Br}$.	I.	Found.	II.
C	42.02	42.3		..
H	3.50	3.6		..
N	10.90			11.2

These results show that the yellow solid is not an unsaturated ketone but *p*-bromphenylmethyl diketone—a mixed α -diketone similar to those made by von Pechmann.

p-Bromphenylmethyl diketone, $\text{BrC}_6\text{H}_4\text{COCOCH}_3$, is a yellow solid melting at 48° . It is almost insoluble in water, but

readily soluble in all common organic solvents. The pure dry solid is stable in the air, but in solution and in the presence of impurities, the substance rapidly combines with oxygen and water, and passes into *p*-brombenzoic acid and acetic acid. In contact with strong aqueous potassium hydroxide it is hydrolyzed to *p*-brombenzoic acid and acetaldehyde, while strong alcoholic potassium hydroxide gives rise to colored condensation products—probably quinones similar to those obtained by von Pechmann from benzoylacetyl.

The *phenylhydrazone* was obtained by boiling an alcoholic solution of the ketone with one equivalent of phenylhydrazine. It is sparingly soluble in alcohol and separates in very thin yellow plates that melt at 199°. Analysis:

0.2467 gram substance gave 0.5088 gram CO₂ and 0.0925 gram H₂O.

	Calculated for C ₁₁ H ₁₃ ON ₂ Br.	Found.
C	56.7	56.3
H	4.1	4.2

As *p*-bromphenylmethyl diketone has carbonyl adjoining a methyl group it readily combines with bisulphites. The addition product with sodium bisulphite is a white, crystalline solid, sparingly soluble in water, insoluble in absolute alcohol. It yields pure diketone when it is suspended in dilute sulphuric acid and distilled with steam. It can, therefore, be used not only for removing all of the diketone from the mixture of products obtained by the action of potassium hydroxide on α -brom-*p*-brompropiofenone but also for determining the amount of diketone formed. In the experiment described above, for example, all the distillates and filtrates were collected, the solvents removed, and the residue shaken for two hours with excess of a saturated solution of the bisulphite. The resulting paste was filtered, the solid washed—first with a solution of bisulphite, then with a small quantity of absolute alcohol, and finally with ether. The ethereal extract of the filtrate was yellow, as was also the residue left after removing alcohol and ether, but tests with phenylhydrazine and potassium hydroxide showed that all of the diketone

had been removed. By repeated distillation of this residue, under diminished pressure, it was separated into two pure products—a colorless solid melting at 48° and a pale yellow liquid boiling at 169° under 15 mm.

The solid was *p*-bromopropiophenone. This was established by comparison with a specimen made from propionyl chloride and brombenzene. It has almost the same boiling point as *p*-bromphenylmethyl diketone and it is equally volatile with steam. When boiled with an alcoholic solution of hydroxylamine it forms an oxime that is readily soluble in alcohol. This oxime separates from hot solutions in long needles that become opaque after removal from the liquid, from cold solutions in thick plates that remain transparent. Both forms melt at 89° . This is 5° higher than the melting point found by Collet, but the analysis shows that the substance was pure. Analysis:

0.2351 gram substance gave 0.4077 gram CO_2 and 0.0878 gram H_2O .

	Calculated for $\text{C}_9\text{H}_9\text{ONBr}$.	Found.
C	47.37	47.3
H	4.39	4.1

The pale yellow oil boiling at 169° (16 mm.) gave the following analytical results:

I. 0.2137 gram substance gave 0.3706 gram CO_2 and 0.0798 gram H_2O .

II. 0.2360 gram substance gave 0.4076 gram CO_2 and 0.2350 gram H_2O .

	Calculated for $\text{C}_9\text{H}_9\text{O}_2\text{Br}$.	I.	Found.	II.
C	47.16	47.3		47.4
H	4.00	4.1		4.2

The substance is α -oxypropio-*p*-bromphenone,



This was established by the following method of preparation: *p*-Brombenzylethyl acetate, $\text{BrC}_6\text{H}_4\text{COCH}(\text{OCOCH}_3)\text{CH}_3$, was made by boiling a solution of α -brompropio-*p*-bromphenone in absolute alcohol with excess of fused potassium

acetate for two hours. It is a very viscous, colorless liquid that boils at 183° – 185° (16 mm.). Analysis:

0.1342 gram substance gave 0.2390 gram CO_2 and 0.0513 gram H_2O .

	Calculated for $\text{C}_{11}\text{H}_{11}\text{O}_3\text{Br}$.	Found.
C	48.70	48.57
H	4.06	4.24

For the purpose of hydrolysis, 20 gram portions of the acetate were boiled for 4 hours with 1 liter of water and excess of freshly precipitated barium carbonate. The resulting liquid was dissolved in ether and the solution dried and distilled under diminished pressure. The product boiled at 169° – 170° (16 mm.) and the distillate was in every way identical with the third substance obtained by the action of potassium hydroxide on α -brompropio-*p*-bromphenone. The oxyketone is a pale yellow, viscous liquid that does not solidify in a freezing mixture. It is less volatile with steam than the two other products of the reaction and it boils at a little higher temperature. As it is readily oxidized by potassium permanganate, it is easy to remove it from the mixture with *p*-brompropio-phenone that is left after treating the entire product of the reaction with bisulphite. It was possible, therefore, to make a fairly accurate quantitative determination of all three of the products.

The procedure was as follows: Two hundred and fifty grams of bromketone were treated with potassium hydroxide and the product distilled under diminished pressure as before. This gave 130 grams of oil, boiling below 180° (18 mm.), and free from *p*-brombenzoic acid. The oil was shaken with 1 liter of a saturated solution of sodium bisulphite for 6 hours. The liquid was then drawn off with the pump, and the solid washed with absolute alcohol and ether. The addition product yielded 51 grams of pure, solid, diketone when suspended in dilute sulphuric acid and distilled with steam. The filtrate from the bisulphite addition product was extracted with ether, then acidified and likewise distilled with steam, but yielded less than a gram more of diketone.

The ethereal extract was dried, the ether and alcohol removed by distillation, and the residue oxidized by shaking with an aqueous solution of potassium permanganate. This left 50.5 grams of *p*-bromopropiophenone which was separated by distillation with steam. Finally, the oxides of manganese were dissolved with sodium bisulphite and sulphuric acid, and the solution extracted with ether. The ether, on evaporation, deposited 26.8 grams of *p*-brombenzoic acid—representing 23.5 grams of oxyketone. The amount of diketone is somewhat less than 1 molecule for 1 molecule of monoketone, but this is to be expected because the latter is unstable in the presence of acids and bases.

II. Experiments with α -Bromopropiophenone.

The reaction was carried out like that with the *p*-brom derivative but as the ketone is readily soluble in alcohol more concentrated solutions could be used. Distillation under diminished pressure gave 210 grams of yellow oil boiling below 140° (16 mm.), from 500 grams of bromketone. This oil contained no phenylvinyl ketone; it did not combine with bromine while the unsaturated ketone combines with it as readily as does benzalacetone. Special tests showed that the oil contained phenylmethyl diketone, propiophenone, and α -oxypropiophenone. The oxyketone was not separated from the mixture but its presence is shown by the fact that the oil contains a pale yellow substance that does not combine with bromine or acid sulphites, but is oxidized by aqueous permanganate to benzoic and acetic acids. A quantitative determination carried out as described in the last experiment with α -brompropio-*p*-bromphenone showed that 200 grams of the mixture contained 82 grams of phenylmethyl diketone, 76 grams of propiophenone, and 42 grams of α -oxypropiophenone. The diketone was identified by its hydrazone, melting at 144° , and its dioxime, melting at 229° . The propiophenone was mixed with a specimen on hand, the mixture solidified by cooling in a freezing mixture, and then allowed to melt; the melting point was the same as that of the components.

III. Experiments with α -Bromisovaleryl-*p*-bromphenyl Ketone.

This ketone, $\text{BrC}_6\text{H}_4\text{COCHBrCH}(\text{CH}_3)_2$, was made from brombenzene and α -bromisovaleryl bromide by the Friedel and Crafts reaction. Although the procedure was the same as that which had given excellent results with other acid bromides, the yield in this case was much smaller—210 grams from 250 grams of bromide. The ketone crystallizes in needles melting at 49° . It is readily soluble in alcohol and ether, moderately in low-boiling ligroin and methyl alcohol. Analysis:

0.1815 gram substance gave 0.2729 gram CO_2 and 0.0359 gram H_2O .

	Calculated for $\text{C}_{11}\text{H}_{13}\text{OBr}_2$	Found.
C	41.25	41.01
H	3.11	3.30

The reaction between potassium hydroxide and this ketone gives no products that do not boil without decomposition under diminished pressure, because the resulting diketone does not have the group necessary for condensation to quinone. The entire product distilled between 165° – 172° (16 mm.). Preliminary tests showed that the yellow distillate contained substances analogous to those obtained from other bromketones. In order to test for unsaturated ketone, some of the oil was dissolved in carbon tetrachloride, the solution cooled to 0° and treated with a few drops of bromine dissolved in the same solvent. The color of bromine remained for an hour. As both mesityl oxide and phenylvinyl ketone under these conditions combine with bromine as fast as it is added, this result proves the absence of unsaturated ketone. The presence of diketone was shown by the oxidation in contact with air, and that of monoketone by oxidation with permanganate and distillation with steam.

As none of the components of the mixture combines with acid sulphites it was necessary to undertake their separation by distillation. Fractional distillation under diminished pressure proved useless; analyses made after 5 distillations showed that the first and last fractions had almost the same composi-

tion. Distillation with steam gave more promising results as the analyses showed that the diketone accumulated in the first fraction. After 6 distillations, carried out like ordinary fractional distillations except that the fractions were collected by quantity instead of boiling point, the first fraction gave results agreeing closely with those calculated for the diketone.

I. 0.1821 gram substance gave 0.3438 gram CO_2 and 0.0737 gram H_2O .

II. 0.2276 gram substance gave 0.4297 gram CO_2 and 0.0920 gram H_2O .

	Calculated for $\text{C}_{11}\text{H}_{11}\text{O}_2\text{Br}$.	I.	Found.	II.
C	51.76	51.49		51.55
H	4.32	4.5		4.55

The yellow liquid had a constant boiling point, 168° – 169° (15 mm.), but it was impossible to prove that it represented a pure substance. As only acid products were left after oxidation with aqueous permanganate it was certainly free from *p*-bromisovalerophenone; but it may have contained the α -hydroxy derivative of this ketone in quantities too small for recognition by analysis. The *dioxime* was obtained by boiling the ketone with an alcoholic solution of hydroxylamine. It separated from alcohol in fine needles melting at 229° . It is moderately soluble in alcohol and ether, insoluble in benzene and ligroin.

Analysis:

0.3855 gram substance gave 35 cc. nitrogen at 22° and 754 mm.

	Calculated for $\text{C}_{11}\text{H}_{12}\text{O}_2\text{N}_2\text{Br}$.	Found.
N	9.82	10.2

p-Bromisovalerophenone, $\text{BrC}_6\text{H}_4\text{COCH}_2\text{CH}(\text{CH}_3)_2$.—The last three fractions obtained by the steam distillation were combined and shaken with a cold aqueous solution of potassium permanganate. This destroyed both the oxy- and the diketone. The unoxidized product was separated by distillation with steam. The ketone solidified in the receiver. After one crystallization from methyl alcohol it melted sharply at 48° .

It crystallizes in large plates that are readily soluble in the common organic solvents.

Analysis:

0.1708 gram substance gave 0.3415 gram CO_2 and 0.0845 gram H_2O .

	Calculated for $\text{C}_{11}\text{H}_{12}\text{OBr}$.	Found.
C	54.78	54.5
H	5.39	5.5

The *oxime*, made by boiling an alcoholic solution of the ketone with hydroxylamine hydrochloride and excess of potassium hydroxide, crystallizes in needles and melts at 91° – 92° . It is readily soluble in alcohol and ether, sparingly in ligroin, insoluble in water.

Analysis:

0.1622 gram substance gave 0.3045 gram CO_2 and 0.0841 gram H_2O .

	Calculated for $\text{C}_{11}\text{H}_{14}\text{ONBr}$.	Found.
C	51.56	51.2
H	5.47	5.8

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
February, 1909.

NOTE ON THE PREPARATION AND THE USE OF ASBESTOS FOR GOOCH CRUCIBLES.

BY PHILIP ADOLPH KOBER.

Although asbestos has been used for Gooch crucibles for some time, yet no standard method of preparation has been adopted. Filter papers for similar purposes, of definite and uniform grades, have been on the market for years. The adoption of a standard, either of asbestos, or of a method for preparing the same, would hasten the day of a more general use of the Gooch crucible.

It is the object of this paper, first, to describe a convenient and quick method of preparation of asbestos, and secondly, to give the possible uses of asbestos, so prepared.

Preparation.—Crude asbestos, obtained from the supply

house, is directly¹ purified by digestion in a strong solution of nitro-hydrochloric acid at a low heat for several hours. After filtering off the acid and washing with distilled water a few times through a Buchner funnel, the asbestos, which at this stage contains mostly large fibres, is transferred to a bottle or cylinder with sufficient water to make a good suspension (2-10 grams per liter). Then, as suggested by Folin,² a strong air current is passed through the suspension for a few minutes (5 to 10 min.).

This agitation is sufficient to tear the crude material into fine shreds, but is not quite sufficient to produce a pulp, emulsive in appearance.

To produce an emulsive-looking pulp, a quality that yields fine asbestos paper, a further treatment is necessary. This consists essentially in filtering the suspension of asbestos, after agitation, through a Buchner funnel (10 cm.) with the aid of strong suction, the perforations of the funnel being kept open by stirring with a glass rod. The filtrate should not contain any large fibres. Large quantities of purified asbestos can thus be prepared in twenty minutes without much manual labor.

Use.—Asbestos pulp, prepared as described above and diluted to about 0.1 per cent, can be used almost as a real solution. After thorough shaking for a few minutes, the amount obtainable by volumetric measurement is, for most analytical filtrations and determinations, a constant quantity. To put this statement in other words, a suspension of asbestos can be obtained which makes it easily possible to control the weight of the asbestos mat. Furthermore, by using the same volume of asbestos solution, and assuming that the crucible does not change materially in weight through use, a Gooch crucible of constant weight is practically obtained.

With an ordinary 2½ liter bottle, having a suitable pipette attached through the stopper, mats were obtained which gave the results shown in columns 1 and 2, when the porcelain crucible (12-14 grams) was weighed before and after the addi-

¹ Cutting or scraping of dry fibre is in this method unnecessary.

² Folin: *J. Biol. Chem.*, 1, 149 (1906).

tion of the asbestos. Substituting an automatic¹ pipette for an ordinary one, mats were obtained which, when removed as asbestos paper, dried, ignited, and weighed, gave the results shown in columns 3 and 4.

Ordinary Pipette.		Automatic Pipette.	
1. Weight.	2. Difference.	3. Weight.	4. Difference.
0.0143	0.00004	0.01535	0.00007
0.0144	0.00014	0.01520	0.00008
0.0142	0.00006	0.01520	0.00008
0.0141	0.00016	0.01535	0.00007
0.0144	0.00014	0.01535	0.00007
0.0142	0.00006	0.01510	0.00018
0.01426 Av.		0.01535	0.00007
0.00010 Av.		0.01535	0.00007
		0.01528 Av. 0.000086 Av.	

A quantitative control of the asbestos is advantageous, as it permits not only the elimination, for technical work, of the first weighing of the crucible, and, for more accurate work, the postponement of the weighing until after the filtration, but also the substitution of a fresh mat for an old one which for some reason or other filters too slowly.²

The details for making the mats, the weights of which are given above, are as follows: To the crucible, fitted directly, or by an adapter, to a suction flask, are added 15 cc. of 0.1 per cent asbestos. After a few drops have filtered through, a slight suction is applied, and maintained until the mat has been formed and all the water has been filtered. A very strong vacuum is maintained for a minute or more, and the asbestos is then washed with several portions of distilled water. After the suction has been interrupted and the filtrate *refiltered* and washed, the crucible is ready for use.

BOSTON, MASSACHUSETTS.

¹ The outlet of this pipette was 0.5 cm. in width.

² It sometimes occurs in making many determinations, especially in physiological chemistry, that a mat will cease to filter in the middle of a filtration.

THE CONDUCTIVITY OF SOLUTIONS OF LITHIUM
NITRATE IN TERNARY MIXTURES OF ACETONE,
METHYL ALCOHOL, ETHYL ALCOHOL, AND
WATER; TOGETHER WITH THE VISCOSITY
AND FLUIDITY OF THESE MIXTURES.

[TENTH COMMUNICATION.]

BY HARRY C. JONES AND EDWARD G. MAHIN.

A large amount of work has been done with the object of learning something about the electrochemistry of organic solvents, and of binary mixtures of these liquids. This is especially true with regard to the relations existing between conductivity and viscosity of solutions in such solvents. A full account of the work which has been done in this laboratory has been published as a monograph by Jones¹ and coworkers, and the electrochemistry of nonaqueous solvents has been extensively discussed by Carrara.²

In the following pages are recorded the results of a few preliminary experiments, which were made with the object of determining whether any essentially new principles were to be discovered by increasing the number of components of a solvent mixture from two to three. It would be, of course, impossible to predict whether or not the mutual action of three solvents upon each other would be the average action of the three possible pairs of components. No extensive study of this matter has, as yet, been made. We have measured the viscosity of ternary mixtures of water, methyl alcohol, ethyl alcohol, and acetone; and the conductivity of lithium nitrate in these mixtures. The materials, apparatus, and method of making the measurements were essentially the same as outlined in earlier articles. The following example will serve to indicate the method of designating the solvent mixtures: "Acetone (75 per cent Methyl Alcohol and Water)" indicates a mixture of solvents made by adding stated amounts (per cent by volume) of acetone to a mixture of methyl alcohol

¹ Carnegie Institution Pub., No. 80 (1907).

² Ahren's Sammlung, 12, No. 11 (1908).

and water which contains 75 per cent, by volume, of methyl alcohol.

Table I.—Conductivity of Lithium Nitrate in Acetone (25 Per Cent Methyl Alcohol and Water).

V.	At 0° % Acetone.				
	0 %.	25 %.	50 %.	75 %.	100 %.
10	27.26	23.08	23.13	25.80	9.67
50	29.41	24.50	26.60	33.10	14.07
100	30.11	26.07	27.37	35.50	18.1
200	31.06	...	...	38.22	23.8
400	31.35	30.18	28.91	40.54	30.6
800	31.62	31.85	29.27	42.03	43.4
1600	32.16	...	29.73	43.21	55.3
At 25°					
10	56.46	48.07	44.78	40.31	10.87
50	61.51	51.65	51.89	55.29	15.64
100	63.53	55.43	53.88	59.78	19.5
200	65.72	...	...	64.80	25.3
400	66.41	64.05	57.42	68.85	32.4
800	66.94	66.63	58.21	71.78	45.5
1600	68.20	...	58.40	73.16	59.8

Table II.—Conductivity of Lithium Nitrate in Acetone (50 Per Cent Methyl Alcohol and Water).

V.	At 0° % Acetone.				
	0 %.	25 %.	50 %.	75 %.	100 %.
10	21.86	22.54	25.15	28.09	9.67
50	23.91	25.55	29.57	37.62	14.07
100	24.79	26.57	31.08	41.25	18.1
200	25.37	27.11	32.55	44.28	23.8
400	25.47	28.70	34.14	47.31	30.6
800	26.10	28.62	34.17	48.52	43.4
1600	26.94	30.26	35.35	50.40	55.3
At 25°.					
10	44.58	43.79	44.42	42.77	10.87
50	49.41	50.18	53.11	58.37	15.64
100	51.44	52.32	55.90	64.40	19.5
200	52.79	53.67	59.02	69.82	25.3
400	53.10	55.05	62.03	74.56	32.4
800	54.32	56.50	64.35	77.97	45.5
1600	56.50	57.95	64.41	80.10	59.8

Table III.—Conductivity of Lithium Nitrate in Acetone (75 Per Cent Methyl Alcohol and Water).

V.	At 0° % Acetone.				
	0 %.	25 %.	50 %.	75 %.	100 %.
10	24.16	26.32	29.56	31.55	9.67
50	27.56	30.99	36.94	44.86	14.07
100	28.67	32.99	38.90	50.16	18.1
200	29.60	34.11	41.90	55.20	23.8
400	29.82	34.75	42.96	58.80	30.6
800	30.62	35.30	44.31	61.75	43.4
1600	31.45	36.71	45.45	64.84	55.3
At 25°.					
10	43.06	44.63	46.21	43.16	10.87
50	49.58	53.29	58.56	63.32	15.64
100	51.96	56.06	62.36	71.28	19.5
200	53.80	59.20	67.37	79.26	25.3
400	54.63	60.23	69.32	84.82	32.4
800	55.72	61.24	71.51	89.78	45.5
1600	58.06	63.88	73.49	94.22	59.8

Table IV.—Temperature Coefficients of Conductivity of Lithium Nitrate in Mixtures of Acetone, Methyl Alcohol, and Water.

In Acetone (75 Per Cent Methyl Alcohol and Water).

V.	At 0° % Acetone.				
	0 %.	25 %.	50 %.	75 %.	100 %.
10	0.0428	0.0433	0.0374	0.0225	0.0049
50	0.0437	0.0443	0.0380	0.0268	0.0045
100	0.0444	0.0450	0.0387	0.0273	0.0031
200	0.0446			0.0278	0.0025
400	0.0447	0.0449	0.0394	0.0279	0.0023
800	0.0447	0.0437	0.0395	0.0283	0.0019
1600	0.0448		0.0386	0.0277	0.0032

In Acetone (50 Per Cent Methyl Alcohol and Water).

10	0.0416	0.0377	0.0314	0.0209	See above
50	0.0427	0.0385	0.0318	0.0221	"
100	0.0430	0.0388	0.0319	0.0224	"
200	0.0432	0.0391	0.0325	0.0231	"
400	0.0434	0.0367	0.0327	0.0230	"
800	0.0433	0.0390	0.0326	0.0243	"
1600	0.0439	0.0366	0.0326	0.0236	"

Table IV.—(Continued.)

In Acetone (75 Per Cent Methyl Alcohol and Water).

10	0.0313	0.0278	0.0225	0.0151	See above
50	0.0320	0.0288	0.0234	0.0165	"
100	0.0325	0.0290	0.0241	0.0168	"
200	0.0327	0.0294	0.0243	0.0174	"
400	0.0333	0.0292	0.0245	0.0177	"
800	0.0328	0.0294	0.0246	0.0182	"
1600	0.0338	0.0296	0.0247	0.0181	"

Table V.—Conductivity of Lithium Nitrate in Acetone (25 Per Cent Ethyl Alcohol and Water).

V.	At 0° % Acetone.				
	0 %.	25 %.	50 %.	75 %.	100 %.
10	19.66	18.74	20.71	23.93	9.67
50	21.03	20.44	23.64	30.73	14.07
100	21.51	21.05	24.61	33.31	18.1
200	22.03	21.70	25.46	35.20	23.8
400	22.20	22.15	25.78	36.74	30.6
800	22.48	22.04	26.38	37.96	43.4
1600	24.54	22.83	26.69	40.74	55.3
At 25°.					
10	46.70	42.51	41.31	39.75	10.87
50	51.11	47.25	47.93	52.10	15.64
100	52.37	48.76	50.12	56.84	19.5
200	54.00	50.42	52.19	60.51	25.3
400	54.60	51.76	52.93	63.21	32.4
800	55.39	51.62	54.17	65.59	45.5
1600	58.59	52.96	54.78	70.11	59.8

Table VI.—Conductivity of Lithium Nitrate in Acetone (50 Per Cent Ethyl Alcohol and Water).

V.	At 0° % Acetone.				
	0 %.	25 %.	50 %.	75 %.	100 %.
10	12.53	15.98	19.85	23.80	9.67
50	13.57	17.89	23.62	32.49	14.07
100	14.02	18.63	25.13	35.90	18.1
200	14.42	19.21	26.13	38.84	23.8
400	14.60	...	26.98	39.67	30.6
800	14.88	19.33	...	43.56	43.4
1600	14.88	20.56	30.23	46.13	55.3

Table VI.—(Continued.)

At 25°.					
10	31.82	34.54	36.95	36.77	10.87
50	35.34	39.43	44.64	51.27	15.64
100	36.56	41.23	47.69	58.06	19.5
200	37.88	42.64	49.88	62.36	25.3
400	38.31	...	51.71	63.83	32.4
800	38.96	44.15	...	68.75	45.5
1600	39.35	45.56	53.86	71.67	59.8

Table VII.—Conductivity of Lithium Nitrate in Acetone (75 Per Cent Ethyl Alcohol and Water).

V.	At 0° % Acetone.				
	0 %.	25 %.	50 %.	75 %.	100 %.
10	12.01	15.84	20.41	23.29	9.67
50	13.80	19.00	26.84	35.29	14.07
100	14.48	20.21	29.06	40.41	18.1
200	15.14	20.92	31.76	44.80	23.8
400	15.41	21.67	32.70	48.43	30.6
800	15.76	22.52	35.55	51.38	43.4
1600	16.10	22.56	35.20	54.01	55.3
V.	At 25°.				
	0 %.	25 %.	50 %.	75 %.	100 %.
10	25.56	29.66	33.32	32.59	10.87
50	29.91	36.32	44.69	50.39	15.64
100	31.64	38.85	48.68	58.35	19.5
200	33.12	40.44	53.90	65.72	25.3
400	33.90	42.11	55.52	71.59	32.4
800	34.88	41.91	57.32	76.39	45.5
1600	35.85	43.97	60.54	81.28	59.8

Table VIII.—Temperature Coefficients of Conductivity of Lithium Nitrate in Mixtures of Acetone, Ethyl Alcohol, and Water.
In Acetone (25 per cent Ethyl Alcohol and Water).

V.	At 0° % Acetone.				
	0 %.	25 %.	50 %.	75 %.	100 %.
10	0.0550	0.0507	0.0398	0.0265	0.0049
50	0.0572	0.0524	0.0411	0.0291	0.0045
100	0.0574	0.0526	0.0414	0.0282	0.0031
200	0.0581	0.0530	0.0420	0.0287	0.0025
400	0.0584	0.0535	0.0421	0.0288	0.0023
800	0.0585	0.0537	0.0422	0.0290	0.0019
1600	0.0555	0.0528	0.0421	0.0288	0.0032

Table VIII.—(Continued.)

In Acetone (50 Per Cent Ethyl Alcohol and Water).

10	0.0614	0.0464	0.0341	0.0218	See above
50	0.0642	0.0482	0.0356	0.0231	"
100	0.0643	0.0485	0.0359	0.0247	"
200	0.0650	0.0488	0.0364	0.0242	"
400	0.0649		0.0367	0.0244	"
800	0.0647	0.0491		0.0231	"
1600	0.0658	0.0486	0.0313	0.0222	"

In Acetone (75 Per Cent Ethyl Alcohol and Water).

10	0.0451	0.0349	0.0253	0.0160	See above
50	0.0467	0.0365	0.0267	0.0171	"
100	0.0474	0.0369	0.0270	0.0177	"
200	0.0475	0.0373	0.0278	0.0187	"
400	0.0480	0.0377	0.0278	0.0192	"
800	0.0485	0.0380	0.0283	0.0194	"
1600	0.0491	0.0379	0.0288	0.0202	"

Table IX.—Conductivity of Lithium Nitrate in Methyl Alcohol
(25 Per Cent Ethyl Alcohol and Water).

V.	At 0° % Methyl Alcohol.				
	0 %.	25 %.	50 %.	75 %.	100 %.
10	19.66	17.76	19.50	24.35	37.62
50	21.03	19.11	21.65	28.13	48.31
100	21.51	19.89	22.46	29.68	52.0
200	22.03	20.19	22.76	31.76	55.1
400	22.20	20.57	23.08	31.32	56.8
800	22.48	20.63	23.39	32.19	59.6
1600	24.54	21.09	23.34	32.73	61.9
At 25°.					
10	46.70	40.13	39.04	41.67	51.31
50	51.11	44.13	44.05	48.85	67.2
100	52.37	45.97	45.81	51.49	72.6
200	54.00	46.48	46.53	53.73	76.8
400	54.60	47.86	47.35	53.94	80.0
800	55.39	48.10	47.96	56.14	83.7
1600	58.59	49.72	47.92	57.59	86.7

Table X.—Conductivity of Lithium Nitrate in Methyl Alcohol
(50 Per Cent Ethyl Alcohol and Water).

V.	At 0° % Methyl Alcohol.				
	0 %.	25 %.	50 %.	75 %.	100 %.
10	12.53	15.35	19.19	25.18	37.62
50	13.57	16.96	21.95	30.04	48.31
100	14.02	17.61	22.87	31.69	52.0
200	14.42	18.02	23.75	32.97	55.1
400	14.60	18.41	24.61	34.18	56.8
800	14.88	18.60	24.98	34.57	59.6
1600	14.88	19.50	25.15	35.48	61.9
At 25°.					
10	31.82	33.24	36.13	41.18	51.31
50	35.34	37.35	41.91	49.48	67.2
100	36.56	39.10	43.87	52.36	72.6
200	37.88	40.08	45.72	54.91	76.8
400	38.31	41.57	47.44	57.06	80.0
800	38.96	41.63	48.06	57.67	83.7
1600	39.35	43.82	48.53	59.61	86.7

Table XI.—Conductivity of Lithium Nitrate in Methyl Alcohol
(75 Per Cent Ethyl Alcohol and Water).

V.	At 0° % Methyl Alcohol.				
	0 %.	25 %.	50 %.	75 %.	100 %.
10	12.01	15.46	20.00	26.46	37.62
50	13.80	17.96	23.82	32.38	48.31
100	14.48	19.03	25.22	34.69	52.0
200	15.14	19.72	26.11	36.17	55.1
400	15.41	20.32	26.77	37.46	56.8
800	15.76	20.55	27.15	38.51	59.6
1600	16.10	20.82	27.54	39.55	61.9
At 25°.					
10	25.56	29.28	34.09	40.91	51.31
50	29.91	34.77	41.20	50.50	67.2
100	31.64	36.93	43.89	54.35	72.6
200	33.12	38.41	45.52	56.89	76.8
400	33.90	39.81	46.82	59.08	80.0
800	34.88	40.52	47.51	60.86	83.7
1600	35.85	41.34	48.39	62.84	86.7

Table XII.—Temperature Coefficients of Conductivity of Lithium Nitrate in Mixtures of Methyl Alcohol, Ethyl Alcohol, and Water.

In Methyl Alcohol (25 Per Cent Ethyl Alcohol and Water).

V.	% Methyl Alcohol.				
	0 %.	25 %.	50 %.	75 %.	100 %.
10	0.0550	0.0504	0.0400	0.0284	0.0145
50	0.0572	0.0524	0.0414	0.0295	0.0157
100	0.0574	0.0524	0.0415	0.0294	0.0155
200	0.0581	0.0521	0.0417	0.0276	0.0147
400	0.0584	0.0530	0.0420	0.0289	0.0172
800	0.0585	0.0532	0.0420	0.0298	0.0162
1600	0.0555	0.0542	0.0422	0.0301	0.0160

In Methyl Alcohol (50 Per Cent Ethyl Alcohol and Water).

10	0.0614	0.0466	0.0353	0.0254	See above
50	0.0642	0.0481	0.0364	0.0258	"
100	0.0643	0.0488	0.0367	0.0262	"
200	0.0650	0.0492	0.0370	0.0266	"
400	0.0649	0.0503	0.0371	0.0267	"
800	0.0647	0.0495	0.0365	0.0267	"
1600	0.0658	0.0499	0.0372	0.0272	"

In Methyl Alcohol (75 Per Cent Ethyl Alcohol and Water).

10	0.0451	0.0358	0.0282	0.0219	See above
50	0.0467	0.0374	0.0292	0.0224	"
100	0.0474	0.0376	0.0297	0.0227	"
200	0.0475	0.0379	0.0297	0.0229	"
400	0.0480	0.0383	0.0300	0.0231	"
800	0.0485	0.0388	0.0300	0.0232	"
1600	0.0491	0.0394	0.0303	0.0235	"

Table XIII.—Viscosity and Fluidity of Mixtures of Acetone, Methyl Alcohol, and Water.

Acetone (25 Per Cent Methyl Alcohol and Water).

% Acetone.	η 0°.	η 25°.	ϕ 0°.	ϕ 25°.	Temp. coef.
0	0.03286	0.01368	30.44	73.11	0.0561
25	0.03386	0.01428	29.53	70.04	0.0549
50	0.02597	0.01209	38.50	82.75	0.0460
75	0.01310	0.00751	76.36	133.22	0.0303
100	0.00429	0.00346	233.21	288.95	0.0096

Table XIII.—(Continued.)

Acetone (50 Per Cent Methyl Alcohol and Water).

0	0.03586	0.01541	27.81	64.89	0.0531
25	0.02850	0.01340	35.09	74.65	0.0451
50	0.01926	0.01514	51.92	99.96	0.0371
75	0.00984	0.00620	101.63	161.40	0.0235
100	0.00429	0.00346	233.21	288.95	0.0096

Acetone (75 Per Cent Methyl Alcohol and Water).

0	0.02461	0.01253	41.64	79.84	0.0463
25	0.01824	0.00990	54.81	101.06	0.0338
50	0.01203	0.00726	83.10	137.79	0.0263
75	0.00705	0.00491	141.76	203.85	0.0175
100	0.00429	0.00346	233.21	288.95	0.0096

Table XIV.—Viscosity and Fluidity of Mixtures of Acetone, Ethyl Alcohol, and Water.

Acetone (25 Per Cent Ethyl Alcohol and Water.)

% Acetone.	η 0°.	η 25°.	ϕ 0°.	ϕ 25°.	Temp. coef.
0	0.05111	0.01745	19.57	57.30	0.0770
25	0.04329	0.01644	23.10	60.83	0.0653
50	0.02856	0.01288	35.02	67.63	0.0487
75	0.01356	0.00770	73.74	129.88	0.0305
100	0.00429	0.00346	233.21	288.95	0.0096

Acetone (50 Per Cent Ethyl Alcohol and Water).

0	0.06949	0.02298	14.39	43.51	0.0643
25	0.04152	0.01693	24.09	79.05	0.0580
50	0.02284	0.01123	43.78	89.05	0.0414
75	0.01047	0.00648	95.54	154.41	0.0246
100	0.00429	0.00346	233.21	288.95	0.0096

Acetone (75 Per Cent Ethyl Alcohol and Water).

0	0.04826	0.01983	20.72	50.41	0.0573
25	0.02807	0.01341	35.63	74.56	0.0437
50	0.01529	0.00853	65.41	117.21	0.0317
75	0.00935	0.00637	106.93	156.87	0.0177
100	0.00429	0.00346	233.21	288.95	0.0096

Table XV.—Viscosity and Fluidity of Mixtures of Methyl Alcohol, Ethyl Alcohol, and Water.

Methyl Alcohol (25 Per Cent Ethyl Alcohol and Water).

% Acetone.	η 0°.	η 25°.	ϕ 0°.	ϕ 25°.	Temp. coef.
0	0.05111	0.01745	19.57	57.30	0.0770
25	0.04851	0.01862	20.61	53.70	0.0642
50	0.03804	0.01702	26.29	58.76	0.0493
75	0.02198	0.01160	45.49	86.24	0.0358
100	0.00857	0.00583	116.71	171.60	0.0176

Methyl Alcohol (50 Per Cent Ethyl Alcohol and Water).

0	0.06949	0.02298	14.39	43.51	0.0643
25	0.04919	0.01994	20.33	50.14	0.0587
50	0.03086	0.01481	32.41	67.52	0.0433
75	0.01928	0.01083	51.88	92.34	0.0311
100	0.00857	0.00583	116.71	171.60	0.0176

Methyl Alcohol (75 Per Cent Ethyl Alcohol and Water).

0	0.04826	0.01983	20.72	50.41	0.0573
25	0.03468	0.01614	28.83	61.97	0.0461
50	0.02337	0.01216	42.86	82.23	0.0369
75	0.01477	0.00880	67.70	113.62	0.0271
100	0.00857	0.00583	116.71	171.60	0.0176

From the results thus far obtained, it would seem that the viscosity and conductivity values in ternary mixtures are about what might be expected from the behavior of solutions in binary solvent mixtures. A series of experiments with a salt, such as potassium iodide, which shows no abnormality in any of the single solvents, would make possible a more exact comparison of experimental with calculated values. More extensive work along these lines, as well as further investigations in binary mixtures, is now in progress in this laboratory.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
May, 1908.

OBITUARY.

JULIUS THOMSEN.

By the death, on February 13th, of Julius Thomsen, less than two years after that of his French rival, Marcelin Berthelot, thermochemistry has lost the second of those two great

men to whose long and fruitful labors it owes chiefly its present important position in our science. Although Thomsen never showed the many-sidedness of Berthelot, did not introduce as many improvements, perhaps, in the methods of thermochemical investigation, yet his results are, in general, far more accurate and reliable. His book, "Thermochemische Untersuchungen," contains the most important thermochemical data on record, and the services he has rendered to science are incalculable.

Born in Copenhagen on February 18th, 1823, unlike most of his contemporaries, he never "wandered" and his native city can claim him wholly as her own, for here he studied, taught, and worked till the day of his death. Beginning as an assistant at the Polytechnik at the age of 21, he remained there till 1856, when he gave up his position to become a gauger. He soon resumed teaching, however, first as a lecturer in physics at the military "Hochschule," and, in 1866, as professor of chemistry at the University, a position which he held till 1891. The following year he became director of the Polytechnik.

From the first, Thomsen was an enthusiastic adherent of the theory of the unity and indestructibility of energy and as early as 1849 he attempted to determine the mechanical equivalent of electrical energy. He worked out some other problems in the field of electricity, among them being the discovery of a new galvanic element which met with considerable success, when, in 1849, a technical problem led him back to chemistry. A peculiar formation of wonderfully pure cryolite had been found in Greenland and it was Thomsen who, by the discovery of the cryolite soda process, made possible the economic utilization of this new mineral. After establishing this industry, he again turned to pure research, taking up, now, the heat changes involved in chemical reactions, and for over thirty years he worked tirelessly on this problem, making enormous numbers of measurements of the heats of solution, combination, and combustion of many compounds. Most of the results of his work were published in the *Berichte* of the German Chemical Society and in the *Journal für praktische Chemie*, and in 1882 were brought together in his monumental four-volume book, "Thermochemische Untersuchungen."

His work did not at once receive the attention and recognition which it merited. In 1877, however, the University of Upsala conferred upon him the degree of Doctor of Philosophy, and two years later that of Doctor of Medicine was given him

by the University of Amsterdam. In 1883 the Davy Medal was awarded to him. He was an honorary member of the German and American Chemical Societies.

C. A. R.

REVIEWS.

LES NOUVEAUTÉS CHIMIQUES POUR 1908. Nouveaux appareils de laboratoire. Méthodes nouvelles de recherches appliquées à la science et à l'industrie. Par CAMILLE POULENC, DOCTEUR ÈS SCIENCES. Avec 200 figures intercalées dans le texte. Paris: Librairie J. B. Baillière et Fils. 1908. pp. VIII + 354. Price, Fr. 4.

The appearance of former volumes of this annual publication has already been noted in THIS JOURNAL. The same general plan as in previous years has been followed by the author. Every one will find it well worth while to at least glance through this book, for a very large number of new forms of chemical apparatus is described.

C. A. R.

DECORATION OF METAL, WOOD, GLASS, ETC. A Book for Manufacturers, Mechanics, Painters, Decorators and all Workmen in the Fancy Trades. Edited by H. C. STANDAGE, Consulting Chemist. New York: John Wiley and Sons. 1908. pp. 228. Price, \$2.00.

This book contains in compact form directions for making and using various preparations for decorating metals, wood, glass, etc. The editor seems to have covered the field very thoroughly.

C. A. R.

TEXT BOOK OF PHYSIOLOGICAL CHEMISTRY IN THIRTY LECTURES. By EMIL ABDERHALDEN. Translated by WILLIAM T. HALL and GEORGE DEFREN. New York: John Wiley & Sons. pp. XIII + 722. Price, \$5.00, net.

An adequate translation of Prof. Abderhalden's text book is entitled to a very warm welcome. The German edition has taken its place in the front rank of the comparatively few text books on physiological chemistry which aim at anything like a philosophical treatment of the subject.

The lecture form of presentation and the mode of treatment in many ways recalls the older work of Bunge and it is interesting to note how enormously the scope of practical investigation and the general stock of facts has increased since the latter volume was published.

Perhaps the most novel portion of the book is contained in the two chapters entitled "Outlook," in which the reader will find much that is helpful and suggestive. Abderhalden develops in a logical fashion a chemical explanation for the conception of species and their maintenance, and shows how morphologically similar organs such as are found in the differ-

ent vertebrates have a chemical composition characteristic for each species and perhaps for each individual. It is interesting to contrast this opinion with diametrically opposite views of Cuvier, who wrote: "It is not in the substance that in plants and animals the identity of species is manifested, it is in the form."¹ Perhaps a compromise between these opposing ideas will be necessary in order to arrive at the truth.

With regard to the translation by Messrs. Hall and Defren, there is little to be said. On the whole, the translation is admirable and the system of spelling adopted for the various compounds is very satisfactory. Although the task of proof-reading was shared by others than the translators, there is room for much improvement in this direction. The repeated use of the word "glucohemia" as the equivalent of "hyperglukämie" appears to be objectionable.

It is unfortunate that many comparatively glaring errors in matters of fact which have been exposed since the book was originally written should not have been corrected in the English edition. For example, it is stated in several places that tryptophane (indole- α -aminopropionic acid) yields skatol-carboxylic and skatolacetic acid through the action of putrefactive organisms, although it has been shown by Ellinger for a comparatively long time that these substances are indoleacetic and indolepropionic acids, respectively. Many other similar examples might be cited, but drawbacks such as these can only slightly detract from the general merit of so important a contribution to biochemical literature.

H. D. DAKIN.

GRUNDLAGEN UND ERGEBNISSE DER PFLANZENCHEMIE. Nach der schwedischen Ausgabe bearbeitet von H. EULER, Professor der Chemie an der Universität Stockholm. Erster Teil: Das chemische Material der Pflanzen. Mit einer Abbildung im Text. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1908. pp. ix + 238. Price, M. 6, unbound; M. 7, bound.

Instead of taking up the entire compass of our knowledge of the constituents of the plant world, a method so admirably used in Czapek's *Biochemie der Pflanzen*, Euler considers in great detail the properties of a much smaller number of the more important classes of organic compounds and their changes.

In the second part, which is to appear later, he will present the physical chemical relationships which are of importance in the plant world, and show the real connection between the chemical and physical chemical facts and the biological results.

¹ *Eloges historiques*, Vol. 3, p. 156.

In this first volume he treats briefly, but clearly, the facts and relationships of such classes of compounds as alcohols, aldehydes, fats, waxes, carbohydrates, quinones, acids in ferns, glucosides, terpenes and complex compounds, resins, alkaloids, purines, polypeptides, proteids, dyestuffs, sulphur and phosphorus compounds, and the contents of the ashes obtained from plants.

S. F. ACREE.

THE BREWER'S ANALYST. By R. DOUGLASS BAILEY, F.C.S., F.R.M.S.
New York: Van Nostrand & Co. pp. x + 423. Price, \$5.

This work, though written primarily for those interested in the chemical problems associated with brewing, will find a use in a much wider field than might be imagined from the title, since it covers topics very extensively studied in both chemical and biological laboratories. It becomes a very useful compendium in any laboratory that deals with the analyses of the products of organic life. It is essentially a discussion of analytical methods, together with a consideration of their application and meaning. The scope of the work may be best understood by a brief review of the subjects treated.

A general consideration of analytical methods as applied to organic products is followed by a somewhat extended consideration of the use of the polariscope and its value in the study of sugars. A chapter on the carbohydrates will be of special value in biological or botanical laboratories, containing, as it does, comparative studies of starches from all the chief sources from which starch is obtained, together with photographs of the numerous types. The chemical nature and behavior of proteids, albuminoids, and enzymes cannot fail to be of great utility to all students who have to deal with these compounds in any chemical relations. The method of preparation of standard and other solutions gives in a condensed manner a type of information that every analyst is constantly desirous of using. An extended summary of the methods of analysis best adapted to the study of organic products occupies nearly one hundred and fifty pages, and contains a large amount of exactly the kind of information that is constantly wanted in any analytical laboratory. An extremely valuable chapter follows upon the interpretation of the results of analysts in determining purity or impurity of the materials examined, giving briefly the accepted conclusions that may be drawn from chemical analyses. While the first 325 pages are thus devoted almost wholly to chemical problems, they are followed by 150 pages which deal with microscopical and biological aspects of all problems related to brewing. Since bacteria, yeasts, and molds are all con-

cerned in brewing problems, this section of the work contains a valuable summary of the methods used in the study of these types of organisms, together with descriptions and figures of the important organisms associated with brewing in all its aspects. Finally, an appendix contains a long list of valuable tables.

For a laboratory dealing with the problems of brewing, this book, of course, has its special usefulness. But chemical, and especially biological laboratories will find much in it of great value. Its careful study of sugars and starches, its consideration of proteids and enzymes, its descriptions of yeasts and methods of their culture, and its valuable tables make it a very useful book of reference for any laboratory or any person dealing in a practical way with the chemical products of the living organism.

H. W. CONN.

QUANTITATIVE ANALYSE DURCH ELEKTROLYSE. VON ALEXANDER CLASSEN. Fünfte Auflage in durchaus neuer Bearbeitung. Unter mitwirkung von H. CLOEREN. Mit 54 Textabbildungen und 2 Tafeln. Berlin: Verlag von Julius Springer. 1908. pp. XI + 336. Price, M. 10.

As is well known, this book, in its present form, is the outgrowth of the author's "Introduction to Quantitative Analysis by Electrolysis," published in 1882. This book has grown with each new edition, as more and better methods have been brought to light. The author tells us that the applications of quantitative electrical methods to both scientific and technical problems have increased so greatly in the last ten years that the present edition can be regarded as an essentially new work.

In studying and applying the various methods discussed in this book, Americans should not forget the splendid work in this field of Edgar F. Smith, which may not always be given the full credit that it deserves.

The application of electricity to quantitative analysis has revolutionized certain phases of this fundamental subject. It has been a comparatively short time since there were only a few metals that could be separated electrolytically. Now the number of such separations that can be effected is so large that metals which cannot thus be separated are the exception rather than the rule. A glance through the "Table of Contents" of this book will verify the above statement.

The work in hand comes from one of the leading authorities in the field, and is, therefore, indispensable to all analysts, whether they are dealing with technical or with scientific problems.

H. C. J.

AN INTRODUCTORY COURSE OF QUANTITATIVE CHEMICAL ANALYSIS. With Explanatory Notes and Stoichiometrical Problems. By HENRY P. TALBOT, PH.D., Professor of Inorganic and Analytical Chemistry in the Massachusetts Institute of Technology. Fifth edition, rewritten and revised. New York: The Macmillan Co.; London: The Macmillan Co., Ltd. 1908. pp. vii + 176. Price, \$1.50.

This edition of Professor Talbot's well-known book has been entirely reset and revised so as to bring it up to date, but in general appearance and contents it differs but slightly from previous editions. As stated by the author in the preface, the book "has been prepared to meet the needs of students who are just entering upon the subject (of quantitative analysis) after a course of qualitative analysis. It is primarily intended to enable the student to work successfully and intelligently, without the necessity for a larger measure of personal assistance and supervision than can reasonably be given to each member of a large class." To this end the directions are given in great detail and are followed by notes explaining the reasons for each step. In the present edition, the ionic changes involved in the analytical procedure under discussion, the bearing of the mass law, etc., have been incorporated in these notes, while a brief discussion of the theory of electrolytic dissociation is retained in the appendix. Under the head of gravimetric analysis are given the determinations of chlorine in sodium chloride, of iron and sulphur in ferrous ammonium sulphate, of phosphoric anhydride in apatite, of lead, copper, and zinc in brass, of silica in silicates, and a complete analysis of limestone; under volumetric analysis are found the determinations of the alkaline strength of soda ash, of iron by the permanganate and bichromate processes, of antimony by means of iodine solution, of available chlorine in bleaching powder by titration with sodium arsenite solution, and of silver by the thiocyanate process. A distinctive feature of Professor Talbot's book is the space devoted to the discussion and presentation of stoichiometrical problems daily met with by the analyst and the solution of which often presents so much difficulty to the beginner until he has thoroughly mastered the underlying principles. The directions throughout are clear and the student is warned at every step against the possible sources of error. The book is undoubtedly one of the best of the many manuals of elementary quantitative analysis which we have.

C. A. R.

POST'S CHEMISCH-TECHNISCHE ANALYSE. Band II., Heft 3. Dritte, vermehrte und verbesserte Auflage. Von PROF. DR. B. NEUMANN. Braunschweig: Vieweg und Sohn. pp. 659-1048. Price, M. 10.

This part deals with the analysis of fertilizers, soils, air,

ethereal oils, leather and tanning materials, glue, tobacco, rubber, gutta percha, and explosives, more than one-third of the volume being devoted to the latter subject.

The presentation of the various topics is admittedly considerably shorter than that in the book of a similar title edited by Lunge, there being usually no alternative method given; the one given may not always be the best, as it probably is not in the case of the determination of ozone in the air and fat in glue. The treatment of some subjects is not strictly in accord with current American practice, as would naturally be expected; the methods employed for the investigation of the other subjects, particularly tobacco, will be found useful.

For those desiring a concise manual of the analysis of these subjects the book would seem to be well adapted.

A. H. GILL.

SYNTHETIC INORGANIC CHEMISTRY. A Laboratory Course for First Year College Students. By ARTHUR A. BLANCHARD, PH.D., Assistant Professor of Inorganic Chemistry at the Massachusetts Institute of Technology. New York: John Wiley & Sons. pp. VIII + 89. Price, \$1.

This is a collection of simple preparations of metals and of metallic salts. It is new in the introduction of questions and exercises, and in the application of the electrolytic dissociation theory and the mass law. The methods themselves are familiar.

The author argues in the preface for the value of such work following the laboratory study of the nonmetals and preceding qualitative analysis, as a means of familiarizing the student with the properties of the metals. He is using the method in his laboratory with good results.

It should be remembered that the great German laboratory teachers of the past—such as Wöhler, Liebig, and Bunsen—required inorganic preparation work. With the general rush to the field of organic chemistry instructors burdened with the daily task of instructing beginners in inorganic chemistry found relief from their burden by dropping all experimental work except analysis, giving the student a laboratory manual and plenty of analyses and leaving him alone.

Many manuals of inorganic preparations have appeared during the last twenty years in Germany and in this country, indicating a general discontent with the method of depending on analysis alone for laboratory practice. No one who has ever seen the eager interest of young students making preparations can doubt the pedagogic value of such work. The questions and exercises in Professor Blanchard's book enhance this value.

E. R.

THE DESIGN AND EQUIPMENT OF SMALL CHEMICAL LABORATORIES. By RICHARD K. MEADE, B.S., Editor of "The Chemical Engineer," Author of "Portland Cement" and "The Chemist's Pocket Manual," Chemist, Dexter Portland Cement Co., etc. Chicago: The Chemical Engineer Publishing Co. 1908. pp. iii + 136. Price, \$2.

This book is designed primarily to be of assistance to young chemists who find themselves confronted with the problem of designing and equipping a laboratory under conditions which may be entirely different from any under which they have before worked. Part of the book appeared in a series of articles in the *Chemical Engineer* during 1905. The fourteen chapters take up General Features, Hoods, Sinks and Water Supply, Desks, Table and Apparatus for Rapid Filtration, Ignition Table and Apparatus for Ignitions, Balance Support, Balance and Accessories, Heating Appliances, Preparation of Distilled Water, Apparatus for Electrochemical Analysis, Sampling Appliances, Assay Furnaces and Accessories, Miscellaneous Laboratory Equipment. The book is copiously illustrated with sample plans of laboratories, cuts of apparatus and laboratory devices, etc. In general, the names of the manufacturers of the various forms of apparatus described are given.

C. A. R.